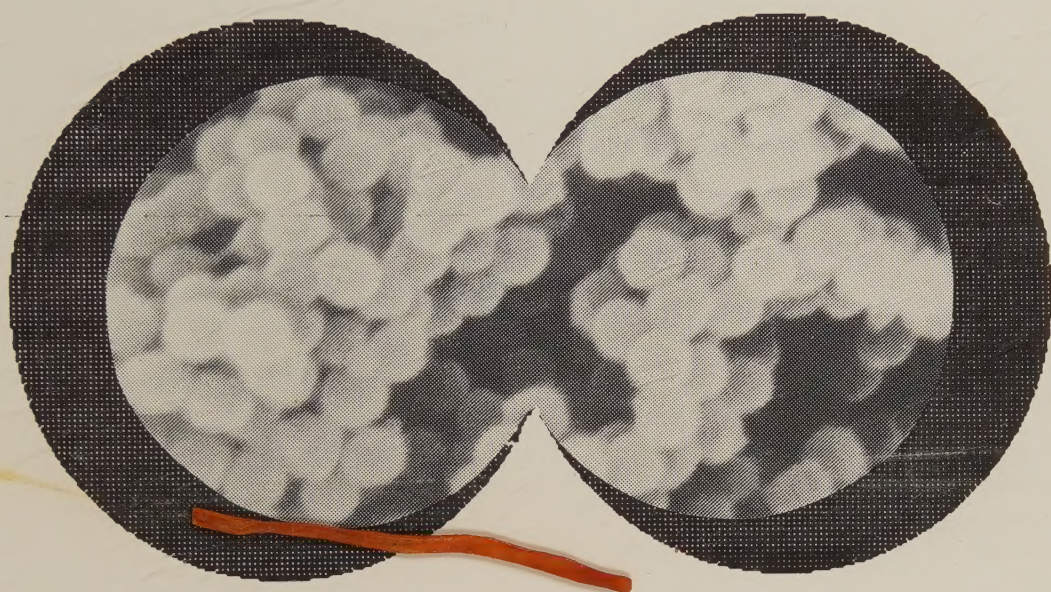


PRIMARY PARTICLES IN VINYL CHLORIDE POLYMERIZATION



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Dissertation
1985

Lund Institute of Science and Technology



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MSc, Ld

A thesis submitted for obtaining a doctorate in technology.

To be presented for public criticism in lecture hall B at the Chemical Centre, Lund Institute of Science and Technology on October 11, 1985 at 10 am.

Faculty opponent Dr D. Rance (ICI). The opposition will be given in English.

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To T. and M.

Organization LUND UNIVERSITY Dept of Chemical Engineering II Chemical Technology P.O.Box 124 S - 221 00 LUND		Document name DOCTORAL DISSERTATION	
		Date of issue June 24, 1985	
		CODEN: LUTKDH/1003 (1985)	
Author(s) Jaan M. Uustalu		Sponsoring organization	
Title and subtitle PRIMARY PARTICLES IN VINYL CHLORIDE POLYMERIZATION			
Abstract Primary particles developed during bulk polymerization of vinyl chloride was found to be formed in two separate stages, a rapid one at the very beginning of the polymerization and a second stage that started as the previously formed particles began to agglomerate. The primary particles stopped growing upon agglomeration. Sorbitan mono laurate decreased the primary particle size by decreasing their colloidal stability. Smaller and less stable primary particles were also obtained when the ionic strength in the monomer phase was increased by addition of tetra-butyl ammonium salts. The free primary particles are electrostatically stabilized. Theoretical relations for electrostatic stabilization was used to calculate the particle stability. These calculations could explain the observed narrow size distribution of the primary particles.			
Key words Vinyl chloride polymerization, poly(vinyl chloride), primary particles, sorbitan esters, particle growth, electrical conductivity, electrostatic stabilization. competitive growth, monodisperse particles.			
Classification system and/or index terms (if any)			
Supplementary bibliographical information			Language English
ISSN and key title			ISBN
Recipient's notes		Number of pages	Price
		Security classification	

Distribution by (name and address)

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INTRODUCTION

Poly(vinyl chloride) (PVC) is a popular engineering polymer but it exhibits many technical obstacles in manufacturing, primarily due to requirements put on the resin morphology. Technical problems arise also from the high vapor pressure and the toxicity of the monomer. Furthermore, processing the thermally unstable PVC into plastic articles depends on many special techniques, unique for the PVC. Disregarding these drawbacks, PVC has found a large market and is presently one of the most popular polymers in plastic engineering today.

Suspension and bulk polymerization are the two main techniques for production of PVC, accounting for about 90 % of all PVC. Resins from these processes are almost identical in appearance. They can be processed in similar ways and may be used interchangeably. A third production method is emulsion polymerization which yields resins completely different in appearance and usage. Suspension and bulk resins are white powders consisting of grains with a typical size of about 150 μm . The grains have an internal porosity which normally amounts to 20-30 %. The internal structure of the porous PVC grain is of decisive importance for the successful processing of PVC (1).

This work is related to the development of the internal structure of the grain at low conversions. The first part of this publication consists of a short literature review of PVC morphology, a brief description of the suspension polymerization process and some references to the analytical techniques which have been used for investigating the PVC morphology. The first part ends with a summary of the findings of the six studies reproduced in the second part of this publication (A-F).

The six investigations describe the formation and behaviour of the so called primary particles, which are formed in the initial stages of polymerization. The stability and agglomeration of these primary particles have a great influence on the development of the PVC internal structure. The studies deal with three different problem areas; the particle formation process (A,B), the influence of additives on the primary particle formation (A,B,C) and the colloidal stability of the primary particles (D,E,F).

An important property of PVC is its insolubility in the monomer VCM. Both suspension and bulk polymerizations are thus precipitation polymerizations, with the formation of a separate polymer phase at very low conversions. The early precipitation of the polymer makes it possible to produce a porous resin. The resin porosity is important partly because a porous structure fuses faster at thermo-mechanical processing than a homogenous product and partly because it makes it possible for a more even distribution of thermal stabilizers. Therefore, the PVC grain internal porosity and particulate nature is one of the most important physical properties for an effective processing of suspension and bulk PVC.

The presence of a porous system in the grains also offers a convenient way to add other additives such as plasticizers, lubricants and pigments. Resins with a high porosity make possible the preparation of dry blends, i.e. large amounts of liquid plasticizers can be absorbed in the porous structure of the resin while the resin still behaves as a dry and free flowing powder. Dry blends are a convenient way of producing flexible PVC articles. During recent years the requirements of almost complete monomer removal have made the PVC porosity an even more important aspect of PVC manufacturing.

The first report of PVC synthesis was given as early as 1872. The polymer was obtained as a insoluble precipitate when sun light acted on vinyl chloride (2). This synthesis of PVC got no greater attention before the late 1920s, when techniques of processing of PVC was developed, partly by use of low molecular weight plasticizers and partly by incorporating vinyl acetate co monomers to the VCM during polymerization. Much effort was made to use PVC as a substitute for rubber, which led to the development of plasticized PVC. Although it did not completely fulfill the requirements as a substitute for vulcanized rubber it showed a great deal of potential. PVC reached world wide use after the second world war, and has since been further developed with an ever improving polymerization and process technique.

The porous structure of the PVC resin was immediately recognized as very important in PVC processing. The intensity of scientific work in the area grew during the 50s and 60s to reach a peak level in the 70s. During the decade 1970-80 there were three international symposia given on PVC, -73 in Toronto , -76 in Lyon and 1980 in Cleveland. Since the Cleveland meeting the activity in scientific work seems to have decreased somewhat. This can be due to the economic strain that almost all PVC producers have suffered.

THE MORPHOLOGICAL STRUCTURES AND THE PRIMARY PARTICLE

The morphological units of PVC have been studied since the beginning of commercial PVC production, and several nomenclatures have been suggested (4,5). The nomenclature given by Sanderson is the one used in this work (6).

Nomenclature of morphological units in PVC

	Name	Approx radius	Approx. conv.
	Polymer molecule	50 Å	≈0%
	Basic particle	15 nm	≈0%
	Primary particle	0.1 μm	0-5%
	Grain	150 μm	0.05%
	Aggregate	0.4 - 2 μm	3%

The polymerization of VCM is initiated by radical producing initiator to the monomer. The primary radicals produced by the initiator decomposition will immediately add to the unsaturated monomer molecule, producing a new radical, often referred to as a monomer radical. The chain reaction continues with addition of further monomer units, forming a oligomeric chain, which at a certain size becomes insoluble in VCM. The oligomeric precipitate is swelled by large amounts of monomer (7), which allows the polymerization to continue in the polymer phase(8).

The molecular size in VCM polymerization is not determined by the rate of termination, but by the rate of radical transfer to monomer. A monomer radical produced by transfer to monomer is the starting point for a new polymer molecule. The new polymer molecule is developed close to the first one. The process of radical transfer is repeated about 5 times before the radical finally is terminated by reaction with another radical (9).

Since most initiator molecules decompose into two radicals is each polymerization event, starting with an initiator decomposition followed by the formation of about 10 polymer molecules. The 10 polymer molecules formed during one polymerization event are closely spaced and will probably agglomerate to form small particles of 15 nm size. These particles are called basic particles (10). Each basic particle exists a short time as there is no force preventing their agglomeration. The particle size therefore, will increase rapidly by repeated agglomeration, until the particle reaches a diameter of 0.1 μ m. At this size the particles become colloiddally stable (10,11). Colloiddal stability means that the particles grow only by absorption of newly formed, colloiddally instable, basic particles. The 0.1 μ m particles which have colloiddal stability are called primary particles. The important differences between the 0.1 μ m primary particles and particles of smaller size are their colloiddal stability and their much lower

growth rate compared to the smaller particles.

The assumption that large numbers of basic particles are initially formed and agglomerate rapidly to form colloiddally stable primary particles is supported by the observation that the initially large number of PVC particles decrease at very low conversion of polymerizations (12,13).

Although the existence of the primary particles have been known for quite a while (12,14), the forces stabilizing these particles have only recently been studied. Studies have shown that the particles are electrostatically charged, which implies that the particles are electrostatically stabilized (15,16,17,18). The colloiddally dispersed particles agglomerate eventually into very porous structures of 100-200 μm size, the PVC resin grains. Inside each grain there exists subunits of about 10 primary particles, which eventually fuse together forming a new morpholigical unit, called an aggregates (6,45). According to older nomenclature these fused aggregates are called primary particles (19). The aggregates grow in size and appear in the final resin as spherically shaped particles with a diameter of about 1 μm . It is these aggregates which build up the PVC grain internal structure. The importance of grain internal structure is evidenced by the intensity of research made, both in relation to processability (20-22) and as a function of polymerization conditions (23-25).

The development of the different morphological units in PVC has been excellently reviewed, by Ugelstad et. al. (8) and by Allsop (19). The morphology of PVC bulk resins have also been invetsigated extyensively by Behrens' research group in GDR (26-30).

SUSPENSION POLYMERIZATION

The development of the morphological units described above are valid for bulk and suspension polymerizations. Suspension polymerization technique is commercially the most important, responsible for almost 80% of the total PVC output.

The basic principle for suspension polymerization is to emulsify the monomer in water with agitation and surface active dispersants. A typical monomer droplet size is 50-100 μm (24,34). The reaction is started with a monomer soluble initiator. The monomer droplet behaves in many ways as a miniature bulk polymerization.

The surface active additives are often divided into primary and secondary dispersants. The primary dispersants are polymeric surface active agents, the most frequently used are methyl cellulose derivatives and poly(vinyl alcohol)s (PVAI). PVAI:s usually has an acetate content of at least 20%. Recent developments have led to the use of PVAI qualities of higher acetate content, making the additive less water soluble. The type of secondary dispersant naturally depends on the primary dispersant used. For methylcellulose primary dispersants, sorbitan esters such as sorbitan monolaurate are commonly used, and for PVAI low molecular weight poly(vinyl alcohol-co-vinyl acetate)s have been used with considerable success. The acetate content of the poly(vinyl alcohol-co-vinyl acetate) secondary dispersant is in the region where most of the dispersant is insoluble in both the water and the monomer.

Industrial research has a very dominant position in the field of PVC polymerization research. Because of this, published studies investigating the effect of different additives on PVC morphology are rare. One of the main morphology/additive related questions are

PVC resin porosity.

The importance of the interfacial tension on resin porosity has raised some interest. Early studies have tried to correlate the surface tension of water solutions of the dispersants to the resin porosity (31). A recent investigation has made a measurement of the interfacial tension between water and VCM (32). Although there seems to be a relation between the surface activity of the dispersants and porosity, it is concluded that the porosity must partly be determined by mechanisms other than by an the interfacial tension effect (39).

The importance of the precipitation and agglomeration process inside the monomer phase in relation to the resin porosity has been discussed on many occasions, but the subject has been mentioned only very briefly in the literature (39)

Most of the investigators who have studied the relation between additives and internal morphology are concerned with the polymeric primary dispersant (23,31,32,35), while little work has been done on the secondary dispersants. The only secondary dispersants investigated have been ammonium laurate (58,59) and sorbitan monolaurate (38,39,40). Sorbitan monolaurate is reported to give smaller primary particles. It has been suggested that the reason for this effect depend both on increased colloidal stability (36,39) as well as on decreased colloidal stability (40) of the primary particles.

Contrary to most primary dispersants, many secondary dispersants are partially soluble in the VCM phase. Thus, the primary dispersants can only influence the resin morphology by processes on the water/VCM interface, while the secondary disperant can affect the polymerization process inside the monomer phase as well. That some additives have a marked effect

on the internal structure of the PVC grain has been demonstrated by Zichy (45).

ANALYTICAL TECHNIQUES

In most cases, the development of PVC morphology has been studied on polymer samples taken at different degrees of conversion. Samples below 50% conversion contain large amounts of free monomer. Since the polymer is plasticized by the monomer the fine structure can easily be damaged by careless monomer removal. The best method to remove excess monomer seems to be by extraction with cold ethanol or methanol (26). After enough monomer has been extracted so that the polymer has passed into the glassy state, the samples can be washed with water and safely freeze dried.

The extraction methods needed to prepare samples from partly polymerized VCM make such investigations a time consuming operation. A much faster investigative procedure is to study the grain development during polymerization by light microscopy (35,47,51) or by macro photography (25,34). This method however, is limited by the magnification power of the microscopes and by the disturbances caused by the change in the reactor geometry needed to make direct observations possible.

For some investigations special techniques have been developed. The polymer precipitation at low conversions has been studied by turbidimetric measurements (11) and by photon correlation spectroscopy (10). The polymerization process has been studied at somewhat higher conversions by a spinning drop apparatus (45). The electrophoretic mobility of the dispersed and electrically charged primary particles has been measured in high pressure electrophoretic apparatuses (46,47).

The morphology of dry PVC samples has been studied by many different analytical methods. The most common methods are mercury porosimetry (41,50) and plasticizer absorption (20), which are measures of resin porosity. Quantitative information about the porous structure may also be gained by measuring the desorption kinetics of a soluble probe gas (42) and by inert gas adsorption measurements (43).

The light microscope can give information about the larger morphological units (44). Electron microscopes have been used with success for investigations of the small morphological units. Transmission electron microscopes (TEM) (48) can be used to detect smaller units than scanning electron microscopes (SEM) (49) due to the greater resolution power of TEM. The use of TEM is hampered by complicated sample preparation and by PVC shrinkage in the high energy electron beam (49). Microscopic methods usually give only qualitative information. A combination of quantitative porosimetric measurements and a qualitative microscopic investigation can be found with the low melting alloy porosimetry measurement (52). This experiment is made at a temperature where the alloy is liquid, but the PVC still is below the glass transition temperature. After determination of the porosity, the sample is cooled below the melting temperature of the alloy and the PVC is removed by dissolution. The resulting metallic structure is investigated in a microscope.

For investigating the smallest morphological units in the PVC, small angle X-ray scattering has been used (53).

SUMMARY OF RESULTS

EXPERIMENTAL METHODS

The development of the internal structure of PVC was followed by studying samples taken from a polymerization reactor at different degrees of conversions. The morphology was studied by SEM, and the specific surface area was measured by BET. Method for correct measurement of the particle size from SEM micrographs was developed (B). The grain formation process was also studied by macro photography (A) and by measurement of the PVC grain sedimentation volume (B). A method for measurement of the electrical conductivity in vinyl chloride was developed, which showed to be useful in understanding the polymerization process at low conversions (D).

THE PRIMARY PARTICLE

The most surprising observation made by studying samples from bulk polymerizations was that the primary particles in agitated polymerizations rapidly reached a particle size which was not exceeded at higher conversions. The primary particle size independence of conversion mean that the polymerization process proceeded by the formation of a large number of new primary particles (A). It was found that the particles stopped growing upon agglomeration and that the formation of new particles was triggered by this agglomeration. Thus, the primary particles were formed in two separate stages during the polymerization (B). One, rapid at the very beginning of the polymerization, and a second formation stage starting when the initially formed particles agglomerated. At high agitation speeds the number of particles formed during the second formation stage soon surpassed the

number of particles formed in the first formation stage. The rate of particle formation in the second stage equalled the rate of primary particle agglomeration. Also, the total number of unagglomerated primary particles was constant during the first few per cent of conversion (B).

The only previous suggestion of a two stage particle formation was given by Boissel and Ficher (11), who observed the presence of small primary particles just after the agglomeration of the initially formed particles.

At slow agitation speeds the particles agglomerated at higher conversions and grew to a larger sizes (A). This observation is consistent with the fact that the particles grow as long as they are colloidal stable (A,B). That the primary particles agglomerate under the influence of the shear field caused by the agitation depended upon the limited colloidal stability of the primary particles. The low colloidal particle stability was also demonstrated by the finding that it was possible to flocculate the particles by shaking a flask containing dispersed particles (D).

The particles were colloidal stable to larger sizes when agitated carefully, but agglomerated at smaller sizes when agitated vigorously. This indicates that the colloidal stability decreased with particle growth. This observation is important when models for particle stability are considered (E).

The main conclusions drawn from the investigation of primary particle formation are that primary particles grow in size as long as they are colloidal stable in the monomer, and that large number of primary particles are formed if the particles agglomerate soon after their formation. The forces responsible for the primary particle stability determine not only the total number of primary particles but also the size of the primary

particles and, to some extent, the geometry of the grains (D). The primary particles in ordinary polymerizations are stable to less than 0.05% conversion (≈ 30 sec), but it is that short period of stability which determines much of the PVC resin internal morphology.

6. ADDITIVES IN THE VINYL CHLORIDE

Addition of Span 20 (sorbitan monolaurate) to bulk polymerizations of VCM produced smaller primary particles in a larger number (B). The smaller primary particles were formed due to particle decreased stability. An earlier agglomeration of the primary particles was also indicated by macro photography (A). The agglomerated primary particle tended to fuse together faster when Span 20 was present than the particles obtained in additive free polymerizations. The increased fusion rate was observed by a fast decrease in the specific surface area and the appearance of large aggregates obtained from the total fusion of primary particles. These aggregates were seen in samples taken at conversions above 3% (B). These aggregates presumably are the origin of the aggregates of 1 μ m size seen in the final resin.

The short period of colloidal stability of the primary particles with addition of Span 20 was mainly an effect of the surface activity of the sorbitan monolaurate. However, dissociated electrolytes, present as impurities in Span 20 contributed partly to the destabilization (C). The sensitivity of the colloidal stability against electrolytes is explained by the electrostatic nature of the primary particle stability (D).

Contrary to the effect of Span 20, addition of secondary dispersant poly(vinyl acetate-co-vinyl alcohol) had no effect on the primary particle stability or its size (A). Addition of

poly(ethylen-co-vinyl acetat) (EVA) and PMMA on the other hand, gave an increased stability to the primary particles. The largest effect was obtained with high molecular weight PMMA. Addition of 0.1% of the high molecular weight PMMA delayed the particle agglomeration from 0.05 to 1% conversion (A). This increased stability was not followed by an increase in the particle size, as should be expected from what was said above (B). In this case new primary particles were formed continuously without any agglomeration of the initially formed primary particles. The grafting of PVC on the PMMA (54) might have an importance in the particle formation process. PMMA has good solubility in VCM, making PMMA/PVC grafts very potent steric stabilizer for the particles.

The stabilizing action of PMMA might be responsible for the improved PVC resin quality when PMMA is added to the first stage of a commercial two stage bulk polymerization process (55,56). The increased primary particle stability by steric stabilization is also claimed to be the main mechanism increasing the resin porosity when a copolymerizable polyethylene oxide is included as an additive (57).

PRIMARY PARTICLE STABILITY

Previous statements on the electrostatic stabilization of the primary particles are based on electrophoretic measurements (47,16,17). The finding that tetrabutyl ammonium tetrafluoroborate and tetrabutyl ammonium chloride were ionically dissociated in VCM enabled other colloid chemical experiments to be made. Thus, the electrostatic nature of primary particle stability could conclusively be demonstrated by the ability of the electrolytes to flocculate stable dispersions of primary particles in VCM (D). Moreover, primary particles obtained from bulk polymerizations in the presence of dissociating electrolytes agglomerated

early, resulting in PVC grains to build up from small primary particles (D).

The ionic strength in pure VCM was estimated to about $1\mu\text{mol/l}$ by comparing the electrical conductivity of the pure VCM with that of tetrabutyl ammonium tetrafluoro borate solutions of VCM (D). This allowed the electrical double layer thickness in VCM to be calculated to about $0.1\ \mu\text{m}$. Using these data the conditions for particle stability in the VCM were investigated (E). Conductivity measurements at different temperatures showed that the ionic strength in freshly distilled VCM was approximately constant between 20 and 50 C and decreased with further increase in temperature (F).

Attempts to calculate the particle colloidal stability was made. In these calculations the DLVO theory for colloidal stability was used, although it was understood that the DLVO theory has limited validity in systems of low charge density (E). The main object of the theoretical calculations was to explain the experimental observations that the particle stability decreased on particle growth and the relatively narrow size distribution of the primary particles.

As previously stated primary particles were formed up to at least 7% conversion. As seen from paper A and B particles formed at the higher conversions were of the same size as those initially formed. This observation implies that the particles have the same stability whether they were formed at high or low conversion. Considering this, it is rather unlikely that the particle stabilizing charges originate from impurities originally present in the VCM, as previously assumed (15-18).

If the electrolytes which give the particles the stabilizing charges are continuously produced, at least some of the basic

particles formed would be carrying one or a few charges. The theoretical calculations showed that agglomeration of weakly charged basic particles with highly charged primary particles leads to a competitive growth mechanism of the primary particles. This mechanism might explain the relative narrow particle size distribution (E).

A production of dissociating electrolytic units during polymerization should be revealed as an increase in the electrical conductivity during polymerization. Contrary to this, the conductivity decreased during polymerization. However, there were some indications that the electrolytes produced during polymerization were bound to the PVC matrix, and thus unable to give an increase in the monomer phase conductivity (F).

7. ACKNOWLEDGMENTS

My gratitude first goes to Prof. Bertil Törnell, my thesis advisor, for innumerable discussions and suggestions of both theoretical and practical importance. I would also like to thank Dr S. Petersson, Mr O. Bjerke and Mr Å. Rynningen (Norsk Hydro), Dr P. Smallwood (ICI) and Dr T. Hjertberg (Chalmers University of Technology for interesting discussions and practical help in the difficult technique of PVC polymerization; Prof. S. Svensson (Lund University) and Dr. G. Bongolo (ICI Speciality Chemicals) for help with the sorbitan surfactants; Dr B. Jönsson (Lund University) for help with the colloid chemical calculations and to Mr S. Kiuru (Lund inst. of Techn.) for skillful measurements of specific surface areas.

Many Thanks are also due to my colleagues at the dept. of Chemical Engineering II for their great support, and I will specially mention Dr H. Nilsson and Dr C. Silvegren, whose work in

the field of PVC polymerization and development of the polymerization equipment has made my studies possible.

I am also in debt to Dr B. Carter, Miss R. Beynon and Mr B. Bitovft for correcting these pages to a language comprehensible for others than just my self.

I am also thankful for the financial support from the Swedish Board for Technical Development.

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Acta Chem Scand **A30** 267 (1982)

The Influence of Additives on the Primary Particle Nucleation and Agglomeration in Poly(vinyl-chloride)

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The formation and agglomeration of PVC primary particles were studied in bulk polymerization experiments. In the absence of additives, the primary particles started to agglomerate at low conversions. The agglomeration conversion, as well as the size of the agglomerated particles, decreased when the agitation speed increased. At the highest speed tested, the agglomeration started already at 0.05 percent conversion. The primary particle size was about 0.16-0.18 μm , and seemed to be constant in the conversion interval studied (up to 5 percent). This indicated that the nucleation rate of primary particles was almost constant and that the growth rate of agglomerated particles was very low. The addition of sorbitan monolaurate produced a decrease in primary particle size. Polymeric additives such as PMMA, EVA, and PVAc stabilized primary particles against agglomeration but had no marked effect on the primary particle size. The monomer-soluble fraction of poly(vinyl alcohol-*b*-vinyl acetate) with high content acetate groups did not affect either the particle size or the agglomeration process.

INTRODUCTION

Although suspension PVC (S-PVC) has been produced commercially since the late 1930s, rather little is known about the physico-chemical basis of the grain formation process. A better understanding of this would be very useful, as the quality properties of S-PVC resins depend to a large extent on grain morphology. In commercial production, resin properties are controlled by the choice of the suspension stabilizers and by the procedures followed during the polymerization.

One of the most important morphological properties is resin porosity. Several studies show that a low interfacial tension between water and monomer gives high porosity (1-3). Experiments in our laboratory showed that the interfacial behavior of commonly used suspending aids was very complicated and could not be characterized by a single interfacial tension value. The aim of this work has been to investigate whether or not additives used in suspension polymerizations might influence the primary particle nucleation and agglomeration by being dissolved in the monomer. The effect of the additives was studied in bulk phase experiments, assuming that the bulk phase would be representative for the interior of the emulsified monomer.

Many papers have been published about the grain formation process (3, 6-8). Extensive studies using optical microscopy have been carried out in stirred reactors (9) and in small quiescent cells (10).

The polymerization process has also been followed by macrophotography (11). Recently, photon correlation spectroscopy has been used to follow the very first part of the polymerization (12). Very few studies, however, have been concerned with the influence of additives on the grain formation process. One of the few exceptions is a study by Saharova, *et al* (13), which shows that the number of primary particles increases with the addition of sorbitan monolaurate. Interesting results have also been published by Zichy (14), which showed that, in the presence of an undisclosed additive, the primary particle identity and spherical shape were retained at least up to 28 percent conversion.

EXPERIMENTAL

The polymerization experiments were performed in a 200 ml glass-walled reactor, similar to the one previously described by Nilsson, Silvergren, and Törnell (15). In this case, the reactor was equipped with a thermistor and a heating element used for calibration purposes. An anchor stirrer was used.

The polymerization experiments were carried out as follows. The chemicals to be used were added to the reactor, which was sealed, washed with nitrogen, and evacuated. The reactor was then immersed in a constant-temperature water bath (59°C) and approximately 120 g freshly distilled vinyl chloride (VCM) was injected. When all addi-

tives had been dissolved and a steady-state temperature was reached, the thermal conductivity between the reactor and the surrounding water bath was determined. A well-defined current through the heating element caused a temperature rise inside the reactor proportional to the thermal conductivity. By measuring the temperature during the reaction, the developed heat, and thus the conversion, could be calculated.

Polymerization was started by injection of lauryl peroxide dissolved in toluene. The initiator concentration was $9 \cdot 10^{-4}$ g/g VCM. Photographic pictures were taken at a minimum interval of 0.02 percent conversion; using a camera equipped with a Nikor $f = 120\text{mm}$ lens and an ultrashort flash (1/40000s), mounted outside the glass-sided water bath. In this way, the presence of grains larger than 0.025mm could be detected.

To sample the reactor content, the agitation was stopped and a tube, connected to a steel vessel, was inserted inside the reactor. The sample was slowly transferred to the vessel, and was cooled to -78°C . The sample was then mixed with equally cold ethanol. The VCM was slowly evaporated while the temperature was allowed to rise. This procedure ensured that the fine structure of the PVC grains was not destroyed (16). When all VCM had been removed, the ethanol was replaced by water, and the sample was freeze-dried. The samples were examined by scanning electron microscopy (SEM) and by BET specific surface measurements.

Solubilities of chemicals in VCM at 20°C were determined gravimetrically using pressurized centrifuge tubes.

RESULTS AND DISCUSSIONS

Substituted celluloses such as Methocel HB (hydroxybutyl methylcellulose), Berol E230, and Berol CST1030 (ethyl hydroxy ethylcellulose) had no soluble fraction in VCM.

In pure VCM, the solubility of Span 20 (sorbitan monolaurate) was 95 percent; the solubility decreased to 85 percent when water was added.

Poly(vinyl acetate) (PVAc) poly(methyl methacrylate) (PMMA) and poly(ethylene-*b*-vinyl acetate) (EVA) were soluble in VCM. The EVA quality used (Levapren 450N) contained a small fraction of insoluble impurity (less than 1 percent). The poly(vinyl acetate-*b*-vinyl alcohols) studied were partially soluble, the soluble content increased with increasing acetate content (Table 1).

Table 1. VCM-Soluble Fraction of Poly(vinyl acetate-*b*-vinyl alcohol) of Different Compositions, at 20°C .

Polymer Gohsenol	Degree of Hydrolysis	Fraction Completely Soluble in VCM
GSS 5311	18	56
GSS 5312	25	13
GSS 5313	34	6
GSS 5314	43	3

Influence of Agitation

In the absence of additives and at a constant stirring speed (600 rpm), the total number of primary particles increased linearly with conversion in the interval 0.1-5.0 percent; see Fig. 1. Except for the sample taken at the lowest conversion (0.05 percent, the primary particle median diameter was approximately $0.17\mu\text{m}$.

On extrapolating the particle number data in Fig. 1 back to zero conversion, a particle number concentration of $2 \cdot 10^{+13}$ particles/mol monomer was obtained. This value corresponds rather well with results obtained by photon correlation spectroscopy, reported by Rance and Zichy (12), who reported a particle number concentration at zero conversion of about $7 \cdot 10^{+13}$ per mole of monomer (polymerization in quiescent state at 35°C).

Samples taken at low conversion revealed that agglomeration of the primary particles was completed surprisingly early. When agitation was stopped at 0.5 percent conversion, the agglomerates sedimented rapidly, leaving a monomer phase showing only a slight turbidity. Macrophotography revealed that agglomerates appeared already at 0.04-0.06 percent conversion (600 rpm). Fig. 6 shows a SEM micrograph of a grain taken at 1 percent conversion. These early agglomerates were, of course, very voluminous, having a bulk density of only 40 kg/m^3 . The occurrence of agglomerates of this type has previously been described by Barclay (4), who reported them to be constant in number after 1 percent conversion.

The result in Fig. 1 reveals that the primary particles initially grow very fast, but also that the growth rate tends to level off at a particle size of $0.16\text{-}0.18\mu\text{m}$. This size is reached at the same conversion (0.05-0.1 percent) at which the agglomeration started.

Some of the polymer formed will, of course, precipitate on the agglomerate. Due to the tendency to minimize the surface area, it will preferentially adsorb at the contact points between the agglomerated primary particles. Particles may also grow because of polymerization in the gel phase. As newly agglomerated particles would be over represented on the surface of the agglomerates, a size difference might exist without being revealed in the SEM mi-

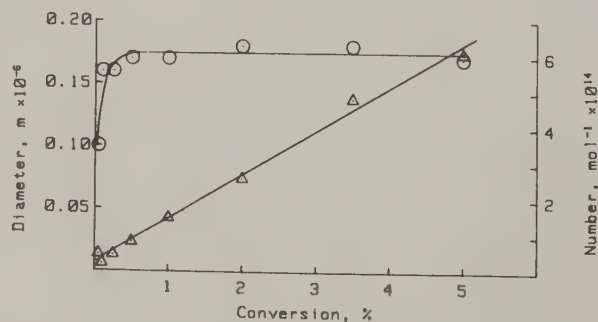


Fig. 1. Primary particle size and number at different conversions; $\circ$ —median particle diameter, $\triangle$ — number of particles per mole of monomer.

crographs. Deposition of polymer between agglomerated particles and growth by gel phase reaction can be seen as a growing gap between specific surface areas calculated from particle size distributions and specific surfaces measured by BET (Fig. 2). At 2 percent conversion, the difference is only a few m^2/g , but at 5 percent conversion, grows so large that half the surface area calculated from particle size measurements was not measured by BET.

The occurrence of grain formation complicated our conversion measurements because the overall heat conductivity decreased rapidly as a consequence of the viscosity increase produced by the particle agglomeration. Conversion values after agglomeration should therefore be considered qualitatively rather than quantitatively.

As could be expected, decreasing agitation speed did lower the tendency for primary particles to agglomerate (Fig. 3). The later grain formation at low agitation speeds was accompanied by an increase in particle size (Fig. 3). This again suggests that particle growth stops as the particles agglomerate. A low agitation speed resulted in a broader particle size distribution.

The large dependence of particle size on agitation might be relevant also to suspension polymerization. It is thus likely that the suspension stabilizers function partly because they affect the shear field inside the monomer droplets. Such an effect can be caused by several different mechanisms.

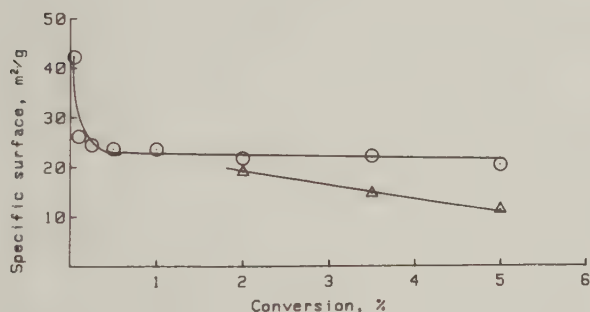


Fig. 2. Specific surface area at different conversions; ○—calculated from particle size, △—BET method.

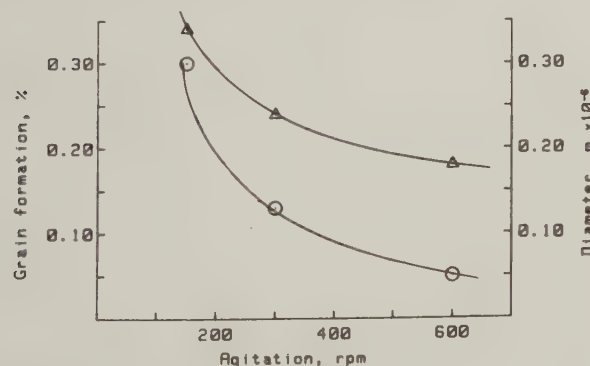


Fig. 3. Primary particle size and grain formation conversion at different agitation speeds; ○—grain formation conversion, △—particle mean diameter.

Influence of Additives

The addition of 0.2 percent Span 20 to the monomer reduced the particle median size at 2 percent conversion to $0.12\mu\text{m}$. This would indicate an even earlier grain formation than in the absence of additives. This was also indicated by the macrophotography results. The conversion could not, however, be measured with enough accuracy. The smaller particle size would predict a specific surface of about $30\text{ m}^2/\text{g}$, but BET measurements at 2 percent conversion gave only $15\text{ m}^2/\text{g}$.

Before polymerization with Span 20, the VCM insoluble fraction must be removed to eliminate wall build-up during bulk polymerization. All work with Span 20 in solution with VCM had to be done fairly rapidly because Span 20 acted as a slow initiator for VCM polymerization.

Addition of EVA increased the stability of the primary particles, seen as a delayed grain formation (Fig. 4). PVAc (Mw 500,000) showed a stabilizing effect of the same magnitude as EVA, increasing the grain formation conversion to 0.08-0.1 percent with the addition of 0.1 percent polymer. Gohsenol GSS 5311 (Mw 20,000), on the other hand, did not show any stabilization with 0.1 percent addition (counted on soluble fraction). The primary particle size was not affected by the addition of EVA or of Gohsenol GSS 5311.

A most astonishing effect on grain formation conversion was observed on addition of PMMA (Fig. 5). This polymer was tested as an example of a basic polymer that would adsorb strongly on the acidic PVC (18). The stabilizing effect of high molecular weight PMMA was 10 times greater than that observed with EVA. At a dosage of 0.1 percent, the grain formation was delayed 20 times. The stabilization was strongly dependent on molecular weight (Fig. 5). When molecular weight was increased from 69,000 to 2,000,000, the grain formation increased more than 5 times.

The addition of high-molecular-weight PMMA did not affect the primary particle size, although the

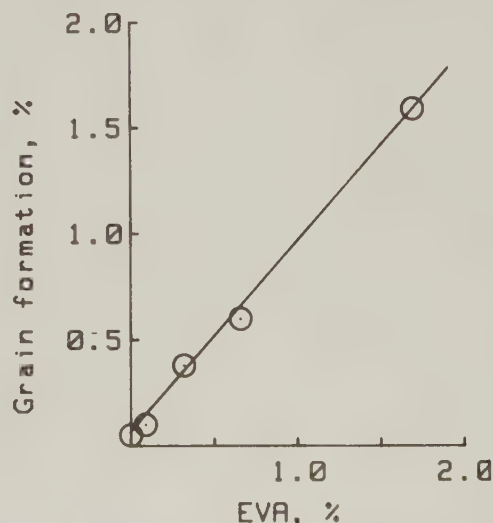


Fig. 4. Grain formation conversion in the presence of EVA.

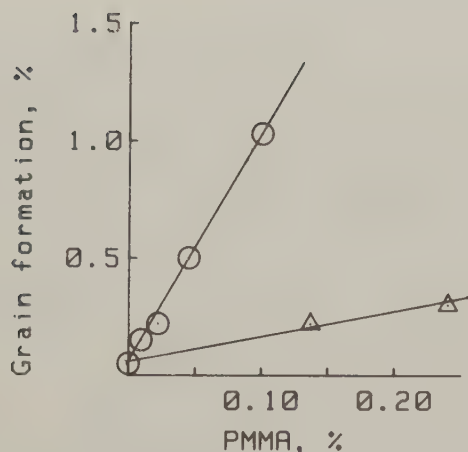


Fig. 5. Grain formation conversion in the presence of PMMA; $\circ$ —MW 2,000,000, $\triangle$ —MW 96,000.

particle size distribution became narrower. This and the similar results obtained with EVA indicated that these polymers acted as sterical stabilizers and delayed the particle agglomeration without affecting the particle nucleation and growth.

The resin obtained at 2 percent conversion by polymerizing in the presence of 0.2 percent high-molecular-weight PMMA gave a specific surface of 22 m²/g. In this case, particle diameter data and the BET method gave identical results. This implies a very slight agglomeration.

Some experiments suggest that small amounts of HCl(g) added to the VCM before initiation have a strong destabilizing effect, indicated by an extremely early grain formation. The primary particle size and the specific surface area of the particles were unaffected. As it has been proposed in several articles that the by-product hydrochlorine is the stabilizing agent for the primary particles (12, 19), it would be interesting to continue these experiments.

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Fig. 6. M-PVC Resin grain at 1% conversion, agitation 600 rpm.

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FORMATION OF PRIMARY PARTICLES IN VINYL CHLORIDE POLYMERIZATION

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INTRODUCTION

ABSTRACT

The formation of primary particles in agitated bulk polymerizations of vinyl chloride was found to proceed in two stages. The first stage occurred at the very beginning of the polymerization; the second stage started as the initially nucleated particles began to agglomerate, and continued up to at least 7% conversion. Upon formation, the primary particles were stable and did not agglomerate until reaching a limiting size, which was found to be lower at higher stirring speeds.

The number of particles formed in the first stage was independent of agitation and other polymerization parameters. The rate of particle formation during the second stage was equal to the rate of particle agglomeration. Thus the total number of primary particles formed was determined almost exclusively by the rate of particle agglomeration.

Addition of the surfactant Span 20 caused an increase in the total number of primary particles. Also, this addition increased the tendency of the particles to fuse together after agglomeration. These effects can be understood to be a consequence of particle destabilization by the surfactant.

When a small amount of a high molecular weight PMMA was dissolved in the monomer, the polymerization behaved quite differently. In this case, the primary particles were prevented from agglomeration, reaching a limiting size independent of stirring speed.

The precipitation of poly(vinyl chloride) (PVC) and the formation of colloiddally dispersed, primary particles begins early in the bulk polymerization of vinyl chloride monomer (VCM). Primary particles are formed by the agglomeration of very small particles, sometimes referred to as basic particles (1). These basic particles have been directly observed in investigations at very low conversion of the VCM (2,3,4). Probably, basic particles are formed by the coagulation of a few polymer molecules, which have been formed close together during a polymerization event involving a number of chain transfer reactions to monomer (1). Since the basic particles have no colloidal stability; they coagulate rapidly to yield particles with an initial diameter of about 80 nm, which are referred to as primary particles in this paper. In a study of quiescent polymerizations, Rance and Zichy found that the primary particles reached a diameter of 90 nm at 0.006% conversion. Furthermore, they found that the primary particles increased in size up to at least 0.1% conversion while remaining constant in number (1). Thus, findings from that study showed that the first stage of primary particle formation is finished before 0.006% conversion.

The primary particles are believed to be electrostatically stabilized by negative charges (3,5). This stabilizing force is weak, and the particles are therefore susceptible to shear-induced agglomeration. Boisel and Fischer showed that, in an agitated reactor, agglomeration occurred at a critical conversion, somewhere between 0.05-0.2% (6). The conversion at which agglomeration began was found to be dependent on the agitation speed (6,7). Agglomeration leads to the formation of

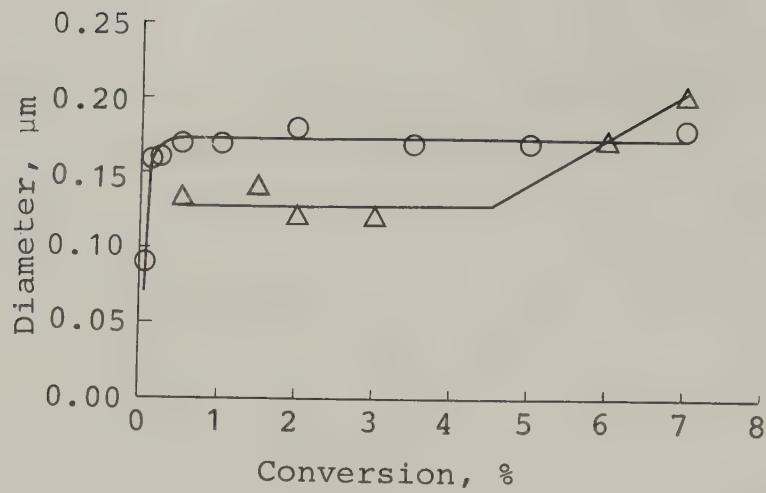


Fig 1. Primary particle size as determined in experiments with an agitator tip speed of 1.5 m/s, (●) without additives, (▲) with 0.2% Span 20.

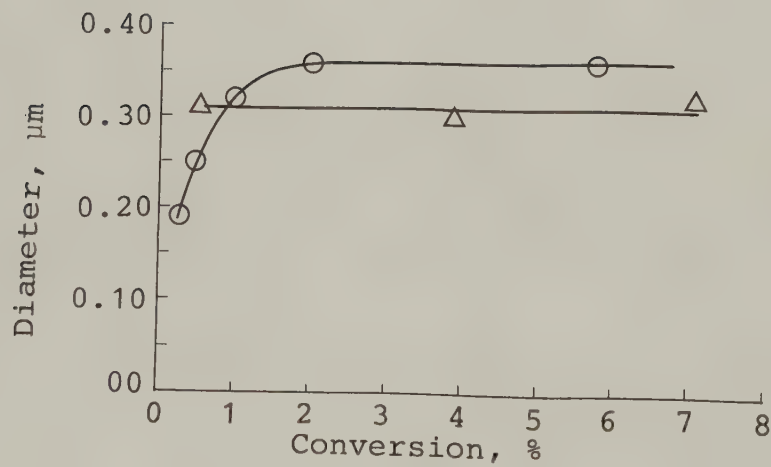


Fig 2. Primary particle size as determined in experiments with an agitator tip speed of 1.5 m/s, (●) without additives and (▲) with 0.2% Span 20.

large granules with a size of about 100 μm . Such granules have been observed at rather low conversions (7).

Zichy has suggested that the primary particles have a tendency to form closely packed clusters containing 13 particles (8). These clusters eventually fuse and grow to a size of about 1-2 μm , which is the approximate size of the structural units in the final resin grains often referred to as primary particles (3).

The purpose of this paper is to discuss the results from an investigation of the formation of primary particles during the second formation stage, and to study the use of sorbitan esters as a mean of controlling the number of primary particles.

EXPERIMENTAL

Polymerization of about 120 g of VCM was carried out at 59 C with 0.11 g of dilauryl peroxide, dissolved in 1 ml of benzene, as initiator. A 200 ml glass-walled reactor with an anchor stirrer was used. The conversion was followed by measuring the thermal power of the process, as described previously (7). The polymerizations could be interrupted at any level of conversion by transferring the reactor contents to a cool steel vessel. The remaining monomer could then be removed by extraction with ethanol (7).

The primary particle size distribution was determined by measuring 80-200 particles from scanning electron micrographs (SEM) taken from 6-10 randomly chosen areas of the sample. The particle size distribution was used to calculate the particle concentration and the theoretical specific surface of the sample. The calculations were made assuming all of the polymer was present as spherical particles, consisting of solid PVC with a density of 1400 kg/m^3 .

The samples investigated in the SEM were coated with 150J Au/Pd to prevent charging. The thickness of the Au/Pd coating was corrected for in the particle size calculations. The accuracy of this correction was tested by coating monodisperse polystyrene latex particles with a diameter of 0.16 μm with different amounts of Au/Pd. Layers of 100, 300 and 400 increased the measured particle diameters by 250, 550 and 900 $\text{\AA}$, respectively. In this case, the particle sizes could be determined with an accuracy of ± 100 $\text{\AA}$. With the PVC samples the accuracy was lower because of a lower micrograph quality. No correction for the possible shrinkage of the PVC particles in the electron beam (25 kV) was made.

The samples for nitrogen BET measurements were dried and degassed in vacuum for a minimum of 24 h at room temperature and then for 2h at 60 C.

The sedimentation volume of the agglomerated primary particles was determined as a function of conversion by measuring the height of the sediment in the reactor when the agitator was stopped during the polymerization. Sedimentation time (period without agitation) was between 60-120 s. The agitator was stopped for less than 6% of the total polymerization time.

The nonionic surfactants Span and Tween (ICI) were used after removal of the VCM insoluble fractions.

RESULTS AND DISCUSSION

Particle formation without additives

During polymerization of VCM without additives, the particles grew rapidly in size at low conversion (Figs.1 and 2), in agreement with previous results (1). Eventually a limiting particle size was reached; over the conversion range studied no particles exceeded that limiting size. At an agitator tip speed of 1.5 m/s, the limiting size was 0.18 μm , reached at a conversion of 0.2% (Fig.1). At the lower agitation speed of 0.4 m/s, the limiting size of 0.35 μm was reached at a conversion slightly above 1 % (Fig.2).

A calculation of the number concentration of particles revealed that, when the particles had reached their limiting size, their total number started to increase (Figs.3 and 4). Thus, a second stage of primary particle formation occurred. The particle concentrations in Figs.3 and 4 refer to the total number of particles, i.e. the sum of free primary particles and primary particles in the agglomerates.

The initial period, during which the particle number was constant, was relatively long at the lower agitation speed (Fig.4). The number of particles present during this period was found to be equal to the number of particles formed in the first formation stage. Close inspection of Fig.3 shows that the particle number curve also has an intercept at the higher stirring speed. This intercept has about the same value as the intercept in Fig.4. The experimental values show that the number of particles formed in the first formation stage to be between 1.2×10^{13} and 4×10^{13}

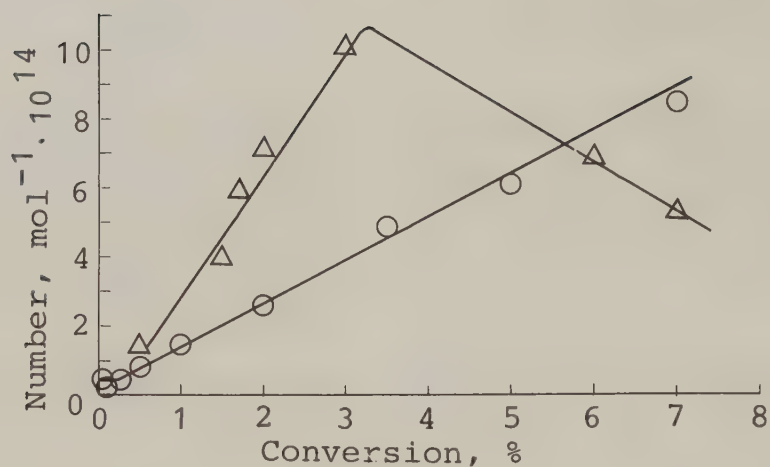


Fig 3. Number of primary particles per mole of VCM found in experiments at an agitator tip speed of 1.5 m/s, (○) without additives and (△) with 0.2% Span 20

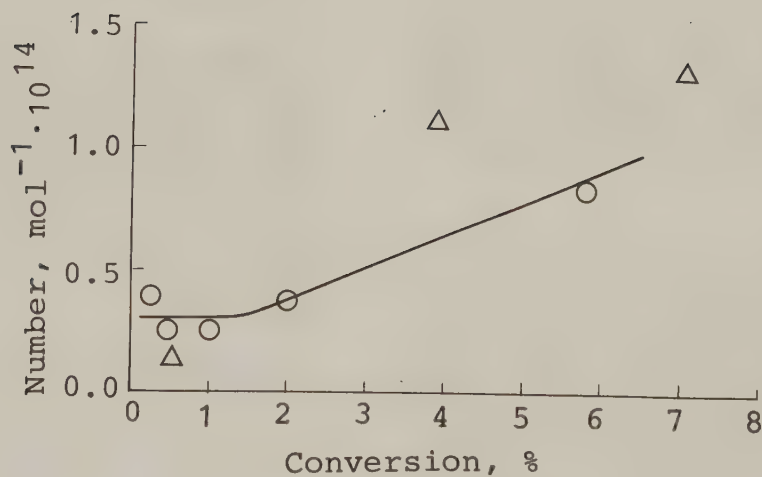


Fig 4. Number of primary particles per mole of VCM found in experiments at an agitator tip speed of 0.4 m/s, (○) without additives and (△) with 0.2% Span 20.

particles/mole. These results are similar to results from a number of other studies, which showed the number of particles at the beginning of the polymerization to be as follows; 4.0×10^{13} (2), 4.0×10^{13} (6) 3.2×10^{13} (11) and 2.0×10^{13} (12) per mole of monomer. The agreement between these studies indicates that the first particle formation stage is controlled by the inherent properties of the system, rather than by the reaction conditions or by the presence of occasionally occurring impurities. So, results from this study and previous show that the number of particles formed in the first stage can only be changed by considerably decreasing the rate of polymerization (6).

The second formation stage

The limiting particle size and the total particle number at a given conversion was found to be strongly influenced by the stirring speed (compare Figs.1 and 3 with Figs.2 and 4). As the figures demonstrate, an increase in stirring speed gave particles with a smaller limiting size and resulted in an earlier start and a higher rate of particle formation in the second formation stage. As a previous study reveals, an increase in stirring speed will lead to an earlier start of primary particle agglomeration (7). Clearly, the different effects produced by changing the intensity of agitation are closely related, and are most probably caused by the increase of the particle's shear sensitivity with particle size. Such a decrease in stability with growth means that, at low stirring speeds, the particles may grow for a longer period and reach a larger size before they become sufficiently unstable to agglomerate. The high shear field developed at a high stirring speed would cause the particles to agglomerate even after a short growing time and, consequently, at a correspondingly smaller size.

Assuming that the primary particles present during the initial period of polymerization are formed at very low conversions, it is possible to understand that particle agglomeration will induce the formation of new primary particles. The primary particles formed in the first formation stage grow by sweeping up basic particles from the monomer phase. Obviously, if the number of primary particles are constant, they must be picking up all the basic particles formed. By this growth process, the primary particles increase in surface area and in their capacity to sweep up new polymer molecules and basic particles from the monomer phase. This stable situation will be disturbed if the primary particles agglomerate. Agglomeration results in an uneven particle distribution over the monomer phase and in the occurrence of volume elements

with a low particle concentration. At a certain level of agglomeration, these volume elements become large enough to permit the formation of new primary particles by coagulation of basic particles. This mechanism is supported by the findings of Boisel and Fischer, who observed that small primary particles appeared after the initially formed primary particles had agglomerated (6).

From this description of agglomeration, it follows that the second stage of particle formation is determined by the rate of agglomeration. Since the number of particles formed in the second formation stage far exceeds the number of particles formed in the first formation stage, it is clear that the total number of primary particles formed in a polymerization process can be varied only by changing the rate of agglomeration. One way of varying the agglomeration rate is by changing the stirring speed; a second is by manipulating the colloidal stability of the primary particles (see below).

Agglomeration and free particle concentration

It has been found that agglomeration of the primary particles by stirring yielded loosely packed grains with a diameter of about $100 \mu\text{m}$ (7). At the highest stirring speed used in this and previous work, 1.5 m/s , agglomerates of $100 \mu\text{m}$ in diameter were observed at conversions below 1%. Upon stopping the stirrer, these agglomerates sedimented rapidly, forming a sharp boundary between the sediment and an upper, slightly turbid monomer phase, which contained unagglomerated primary particles. This sedimentation shows that grains of an appreciable size were formed very early during polymerization and that small aggregates were absent or very few in number. In an experiment at the high stirring speed, the upper monomer phase obtained after sedimentation of the agglomerates was withdrawn and analyzed. It contained 0.14% PVC in the form of primary particles with an average size of $0.16 \mu\text{m}$, in comparison with the overall average particle size of $0.18 \mu\text{m}$. These results indicate that the number of unagglomerated particles was $2.3 \times 10^{13} \text{ mol}^{-1}$, a figure in agreement with the number of primary particles formed in the first formation stage. This concentration of unagglomerated particles, at 1% conversion suggests that the concentration of free, unagglomerated particles remains constant during the polymerization process. Hence the rate of particle formation during the second nucleation stage is equal to the rate of agglomeration. The

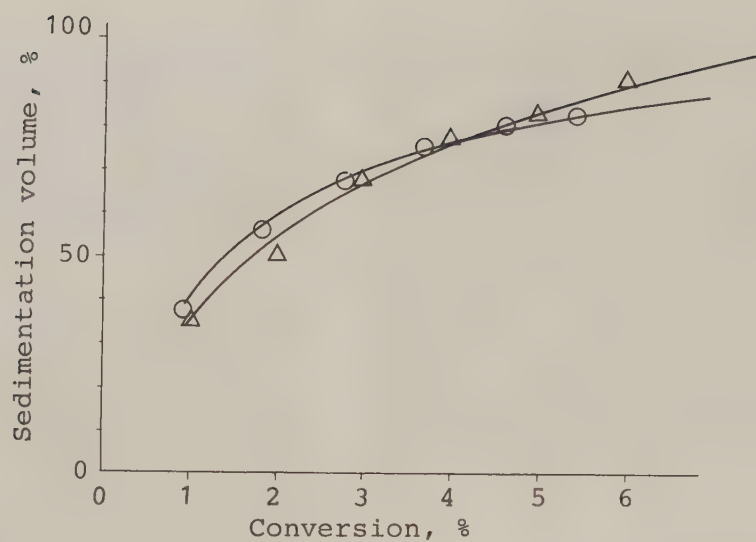


Fig 5. Sedimentation volume of agglomerates as determined in experiments (O) without additives, and (Δ) with 1% Span 20, at an agitator tip speed of 1.5 m/s.

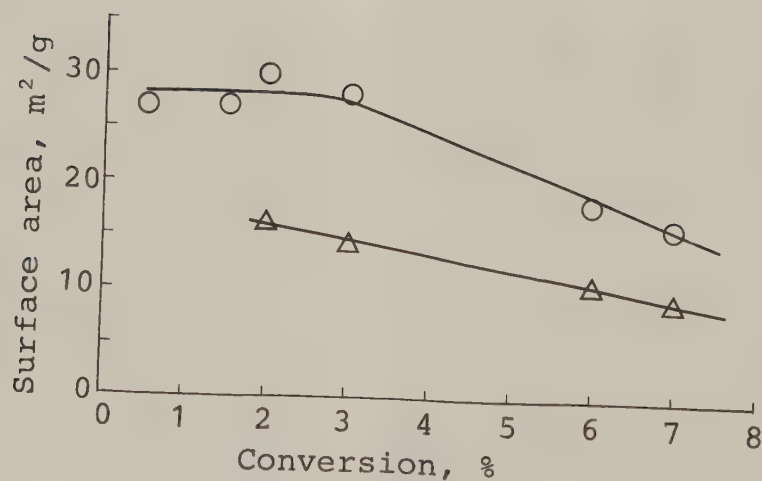


Fig 6. Specific surface of the polymer obtained in experiments at a agitator tip speed of 1.5 m/s, and in the presence of 0.2% Span 20; (O) calculated specific surface, (Δ) BET.

results from these experiments also support the view that the second formation stage begins due to primary particle agglomeration.

Fig.5 gives the sedimentation volume of the agglomerated particles as a percentage of the total volume. The sedimentation volume results are from experiments made at the high stirring speed. The sediment volume is slightly lower than 40% at 1% conversion and asymptotically approaches 100 % at about 7% conversion. Within the conversion interval from 1 to 7% conversion, the grain size was found to be about constant at 100 μm . This means that the rapid increase in the sediment volume observed between 1 and 5% conversion (Fig.5) must be due to the formation of new grains. This conclusion is not in agreement with results reported by Barclay (13), which indicated that new grains are not formed above 1% conversion.

The limiting particle size

As discussed in the previous section the primary particles were found to grow until they eventually became unstable and formed agglomerates. This agglomeration occurred as the particles reached a certain limiting size, which was smaller at the high stirring speed (Fig.1). The particle size data at conversions beyond the bends in the particle size curves in Figs.1 and 2 refer mainly to agglomerated particles. Thus, these results imply that particle growth appeared to stop at particle agglomeration.

Why the agglomerated particles did not grow, or grew at a much lower rate than the free unagglomerated particles., can be explained in several ways;

#1/ Agglomerates move at a lower speed than unagglomerated particles. A particle in an agglomerate thus passes through a smaller liquid volume than a free particle, resulting in a lower absorption rate of polymer from the monomer phase.

#2/ In the agglomerate, the individual particles compete with each other in attracting basic particles from the surrounding liquid phase.

#3/ Basic particles formed in the proximity of agglomerated particles tend to coagulate in the contact zones between particles, thus maximizing the gain in surface free energy. Deposition of polymer in this way was not recorded as particle growth in the SEM micrographs, as the particle diameter was measured in a direction where the particles made no contact with other particles

#4/ As the total number of particles increases with conversion, the growth rate of the individual particles should decrease with conversion, making

it increasingly difficult to detect particle growth.

The importance of the second explanation of the nongrowth behaviour of the agglomerated particles can be understood by a simple calculation. The particles grow by two mechanisms: (i) by absorption of polymer (basic particles) from the monomer phase; and (ii) by polymerization inside the particles. Because of the gel effect, the specific rate of polymerization inside the particles is about 15 times faster than that in the liquid phase (18). If the concentration of unagglomerated primary particles is $3 \times 10^{13} \text{ mol}^{-1}$, the average distance between neighbouring particles will be 1.5 μm . Therefore, a free primary particle is capable of collecting basic particles formed within a distance of 0.75 μm . Assuming that agglomerated particles also grow by absorbing basic particles formed within a distance of 0.75 μm , the calculation of the relative growth rate of free particles and particles in agglomerates of different geometries is possible. Such calculations showed that the rate ratio of volume growth for free particles; particles in a row; very densely packed agglomerate where the growth is dominated by gel phase polymerization, would be 39:5:1. The packing density in a real agglomerate would, of course, be lower than in a densely packed agglomerate, but higher than in a linear row of particles.

The importance of coagulation in the contact zones between agglomerated particles, covered in the third explanation of the limited growth rate of agglomerated particles, was previously demonstrated by comparing the theoretically calculated specific surface of the PVC particles with that determined experimentally by BET (Fig.6) (7).

In addition to the explanations considered here, it is possible that there are further reasons why growth of unagglomerated particles is favoured over the growth of agglomerated particles. For example, if a sizeable fraction of the basic particles were charged, they would tend to coagulate with unagglomerated primary particles rather than with agglomerated particles, which have an overlap of the repulsive electrostatic fields.

The particle stability

The size and number of primary particles formed is determined by the colloidal stability of the particles. It is thus of interest to study if the stability of the particles were affected by the presence of initiator residues at the particle surface or when polymer tacticity is changed. The polymer tacticity affects the solution properties of the

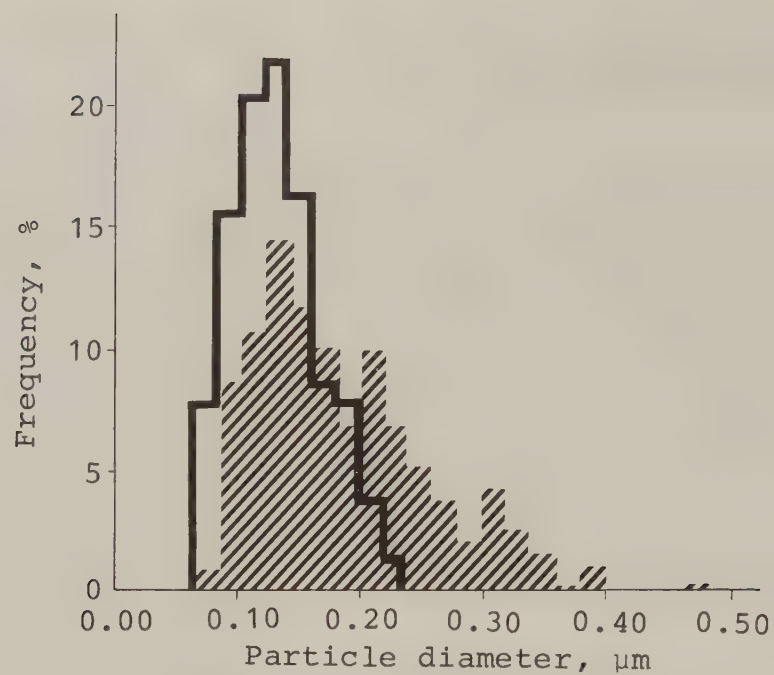


Fig 7. Primary particle size distribution as determined at 2 and 7% (shaded) conversion. Agitator tip speed 1.5 m/s.

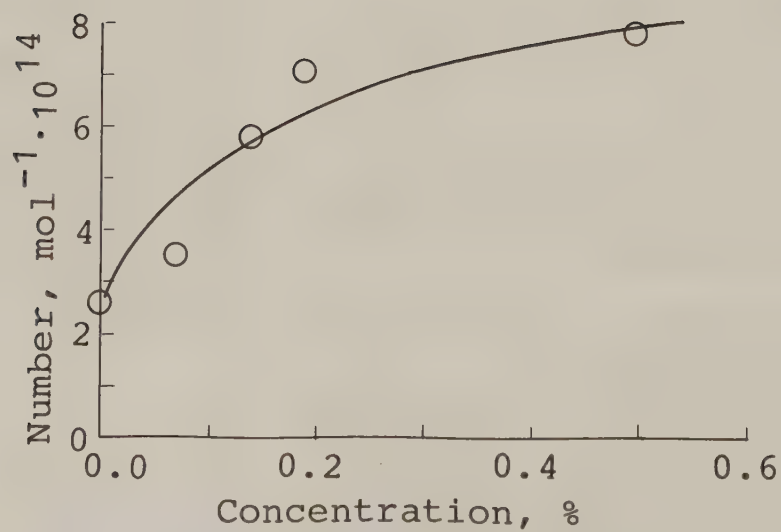


Fig 8. Number of primary particles per mole of VCM at 2% conversion on addition of Span 20.

polymer in its monomer (19). If the particle stability were due to steric stabilization by atactic chain segments sticking out from the particle surface into the monomer phase, the polymer tacticity might effect the particle stability.

To study these effects, bulk polymerizations were carried out with azo-bis-isobutyronitrile and dicetyl peroxy dicarbonate as initiators, in addition to dilauryl peroxide. Experiments were carried out at temperatures between 40 and 60 C using initiator concentrations which gave the same polymerization rate in all experiments. The stirring speed was 1.5 m/s and the particle size was determined on samples taken out at 1% conversion. Differences in primary particle size were not observed in these experiments. Thus it was concluded that, initiator fragments or polymer tacticity have little or no effect on the colloidal stability of the primary particles.

The main reason for particle stability therefore would appear to be electrostatic stabilization, caused by the presence of negative charges on the particles (1,3,5).

Previous work suggests that the negative charges on the particles are due to chlorine ions, which originate from hydrochloric acid formed by reaction between vinyl radicals and oxygen. Since the oxygen concentration would be very low even after a short time of polymerization, chlorine ions from this source could not stabilize particles formed at higher conversions. As seen in this investigation, during the second formation stage the particles grew to the same size as those nucleated initially. This means that the particles obtained in the second formation stage would be equally stable as those obtained in the first formation stage. Hence, it is logical to assume that the polymerization process causes the charges to be formed continuously. One possible source of HCl could be from radical transfer to polymer. Hydrogen abstraction by chlorine radicals occurs with a frequency of 1-3 events per 10 000 monomer units polymerized (17).

Influence of Span 20

The presence of Span 20 during polymerization was found to give smaller primary particles (Figs.1,2) in a correspondingly higher number (Figs.3,4). It follows from the previous discussion that Span 20 must reduce the colloidal stability of the particles. The mechanism by which Span 20 reduces the particle stability is not understood. Furthermore, it should be noted that the conclusion that Span 20

reduces the stability of the primary particles conflicts with the previous assumption that Span 20 increases particle stability (9,10,12).

The specific surface area of the polymer phase decreased rapidly with conversion for the polymer prepared in the presence of Span 20 (Fig.6). The specific surface reduction of polymers prepared in the presence of Span 20 was much larger than for polymers without additives (7). Therefore, particle fusion occurred much more rapidly when Span 20 was present during the polymerization. And it is possible that the more rapid particle fusion in the presence of Span 20 resulted from a reduction in particle stability. A more rapid fusion would be expected if the agglomerates were more densely packed, i.e., in a way which gave increased number of particle-particle contacts. The reason for particle fusion are as yet slightly unclear. Particle fusion could be due exclusively to precipitation of polymer in the contact zones between the particles. However, fusion could also result, if the coagulated particles are forced closer together.

A difference in the packing density or porosity of the grains formed in the presence of Span 20 was not observed in the sedimentation volume measurements (Fig.5).

The relatively rapid particle fusion observed in the presence of Span 20 may lead to an overestimate of the particle number as calculated from particle size data. If the particle fusion observed were due to precipitation of polymer in the contact zones, and if each particle had four contact zones, then a decrease in the specific surface area of 50% would yield an estimate of the particle number too high by 30%. Although not insignificant this error is still too small to invalidate the conclusion that the addition of Span 20 leads to an increase in the total number of primary particles.

In polymerization experiments carried out in the presence of 0.2 % Span 20, 6.8×10^{14} particles per mole were found at 2% conversion. In comparison, 2.7×10^{14} particles per mole VCM were found at 2% conversion in the additive-free polymerization. An increase in the concentration of Span 20 above 0.2% produced no further increase in particle number (Fig.8).

When polymerization was carried out at high stirring speeds and in the presence of Span 20, an increase in the average particle size was observed at conversions above 3% (Fig.1). As the particle size distribution seen in Fig.7 shows this increase was due to the formation of a fraction of large particles with diameters of about 0.3 and 0.4 μm . Clearly these large particles were formed by fusion of

Table 1

Average primary particle size (d) as determined at 2% conversion, in bulk polymerization experiment with and without additives.

Additive	conc. %	d μm
none		0.18
Span 20	0.14	0.13
Span 80	0.14	0.16
Tween 21	0.13	0.16

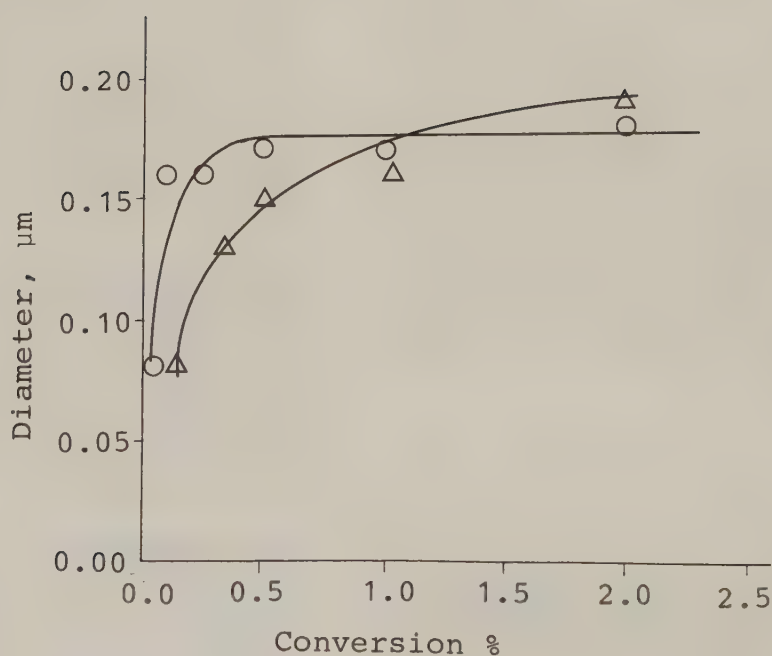


Fig 9. Primary particle size, as obtained (Δ) with and ($\bigcirc$) without the presence of 0.2% PMMA. Agitation 1.5 m/s.

smaller particles, since the total particle number decreased at conversions beyond 3% (Fig.3). Possibly, the large particles were formed by fusion of particle clusters composed of 13 primary particles as discussed by Zichy (8). Such 13 member clusters of 0.12 μm particles would have a size between 0.29-0.36 μm , depending on whether the space between the agglomerated particles were filled with new polymer or if the particles disappeared by coalescence. The distribution in Fig.7 shows that most of the large particles had a size within these boundaries. This type of fusion process, giving rather large particles, presumably was also occurring when the polymerization was carried out in the absence of additives, but than at conversions above 7%.

The effect of other sorbitan esters has also been tested (Table 1). Tween 21 is tetraoxyethylen sorbitanmonolaurate. Span 80 is described as sorbitan mono-oleate, an unsaturated compound, which may be grafted onto the polymer during polymerization. These sorbitan esters were found to affect the particle limiting size in a way similar to that of Span 20, but to a lesser degree.

Influence of PMMA

It has been reported that the addition of PMMA with a high molecular weight gives primary particles with increased resistance to agglomeration (7). At a concentration of 0.2% PMMA the particles remained colloidally stable up to about 2% conversion at an agitator tip speed of 1.5 m/s. According to the mechanism described above, these conditions should yield very large particles and no secondary particle formation at conversion below 2%, but this was not the case. In the presence of PMMA, the particles reached a limiting size, of 0.19 μm , at an agitator tip speed of 1.5 m/s (Fig.9). However, at the lower agitator tip speed (0.4 m/s) and at 1% conversion, the particles had a diameter of 0.21 μm ; they were considerably smaller than those obtained under similar conditions, but in the absence of PMMA. Thus, when PMMA is present, the mechanism of primary particle formation must be completely different from that in absence of PMMA. Possibly, particle nucleation in the presence of PMMA is controlled by grafting of PVC to the PMMA molecules and PMMA acts as a steric stabilizer.

ACKNOWLEDGMENT

We are very grateful to Dr Sven Pettersson and Mr Odd Bjerke at Kema-Nobel AB (presently Norsk Hydro Plast AB) for giving us useful advice and

supplying us with chemicals. We would also like to thank Peter Smallwood, ICI for valuable comments on this manuscript. This work has been partially supported by the National Swedish Board for Technical Development.

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VINYL CHLORIDE BULK POLYMERIZATION IN
THE PRESENCE OF PURE SORBITAN
LAURATES

by

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ABSTRACT

The destabilization of the electrostatically stabilized primary particles in the bulk polymerization of VCM by the addition of Span 20 was found to depend primarily on the surface active surfactant and secondarily on the presence of electrolytically active impurities in Span 20.

Solubility studies showed that the solubility of Span 20 in the VCM phase, at conditions similar to suspension polymerization, was 67%.

1. INTRODUCTION

Nonionic surfactants described as sorbitan monolaurates are frequently used in the suspension polymerization of vinyl chloride (VCM). This surfactant is marketed under many different trade names but for suspension polymerization of PVC Span 20 (ICI) is the most well known.

In the suspension polymerization of VCM, Span 20 is generally believed to be a porosity increasing agent (1). The Span 20 HLB value of 8.4 (2) suggests that this surfactant is predominantly present in the VCM phase. It is further reported that Span 20 can influence the morphological structure of PVC grains during initial stages of bulk polymerization (3,4).

The analysis of experiments using Span 20 is complicated by the heterogeneous composition of the surfactant. Span 20 is produced from coconut fatty acids and sorbitol. The lauric acid content of the fatty acid is only about 50 % (5), and the dehydration of sorbitol to sorbitan gives two different products, the monoanhydrosorbitol and dianhydrosorbitol (isosorbit).

The first main morphological units developed in the VCM bulk and suspension polymerizations are the primary particles, which are formed at a size of about 100 nm (6). The particles grow in size during a brief period, the growth is accompanied by a decrease in their colloidal stability and agglomeration. The particle growth virtually ceases after agglomeration (4,7). Agglomeration of primary particles is followed by formation of new primary particles (8). The appearance of small primary particles is an indication of an early agglomeration of particles with decreased stability. The primary particles colloidal stability depend on their electrical charges (9,10,11).

The purpose of this investigation was to synthesize some of the major compounds in the Span 20 and to determine how these substances affect the primary particle stability.

2 EXPERIMENTAL

The synthetic work was aided by the samples of 1,4-anhydrosorbitol and 1,4-;3,6-dianhydrosorbitol, kindly supplied by ICI/Atlas Chemicals. The sorbitan's were dissolved at 0 °C in pyridine to a concentration of 1%, and lauric acid chloride was slowly added. The reaction products were

separated in a preparative silica gel column, and their purity was tested by GC/MS.

The solubility of Span 20 in VCM was determined at room temperature in 10 ml centrifuge tubes, which could be pressurized. After centrifugation the VCM phase could be withdrawn, the VCM was evaporated, and the amount of Span 20 in solution measured gravimetrically.

The polymerization of VCM and the analysis of the PVC was achieved as described previously (4,7).

The electrical conductivity of the VCM phase was measured at room temperature in a 500 ml stainless steel vessel with circular stainless steel electrodes. The cell constant was 0.0035 cm^{-1} . Conductivities down to 3.8 nS/cm ($10^{-9} \text{ ohm}^{-1} \text{ cm}^{-1}$) could be measured.

3 RESULTS AND DISCUSSION

3.1 Solubility of Span 20

Mixtures of Span 20 in VCM were turbide, due to an insoluble fraction of Span 20. At low Span concentrations, the insolubles formed a relatively stable dispersion, which could be sedimented by centrifugation, whereas, at higher Span concentrations the insoluble part sedimented spontaneously. Five per cent of the Span was insoluble in pure VCM (Fig 1).

Adding small amounts of water decreased the Span solubility in VCM (Fig 1). The solubility fell from 95% to 85% when 0.3 g of water per 1.0 g of Span 20 was added.. Additon of water, above 0.3g/g Sapn 20 only slightly altered the Span solubility. Samples with water contents below the 0.3 water/Span value separated after centrifugation into two phases with the water/Span phase at the bottom. Samples above the 0.3 point separated into three phases, with a Span 20 rich phase in the middle and an nearly pure water phase at the bottom.

The scattering of the solubility data seen in Fig 1 did not depend on the Span 20 concentration, which varied between 1 and 10%. The Span 20 solubility in this low water concentration region, reflects a fractioning of different components in Span 20.

In a mixture of Span, VCM and water with weight ratios of 1:263:192, 67% of the surfactant dissolved in the VCM phase, independent of whether Span was initially dissolved in VCM or emulsified in the water. In these experiments the amounts of Span, water and VCM was close to the conditions of a suspension polymerizations. Therefore, this value of Span solubility in VCM should permit a realistic estimate of the partition of the surfactant during the initial stages of suspension polymerizations.

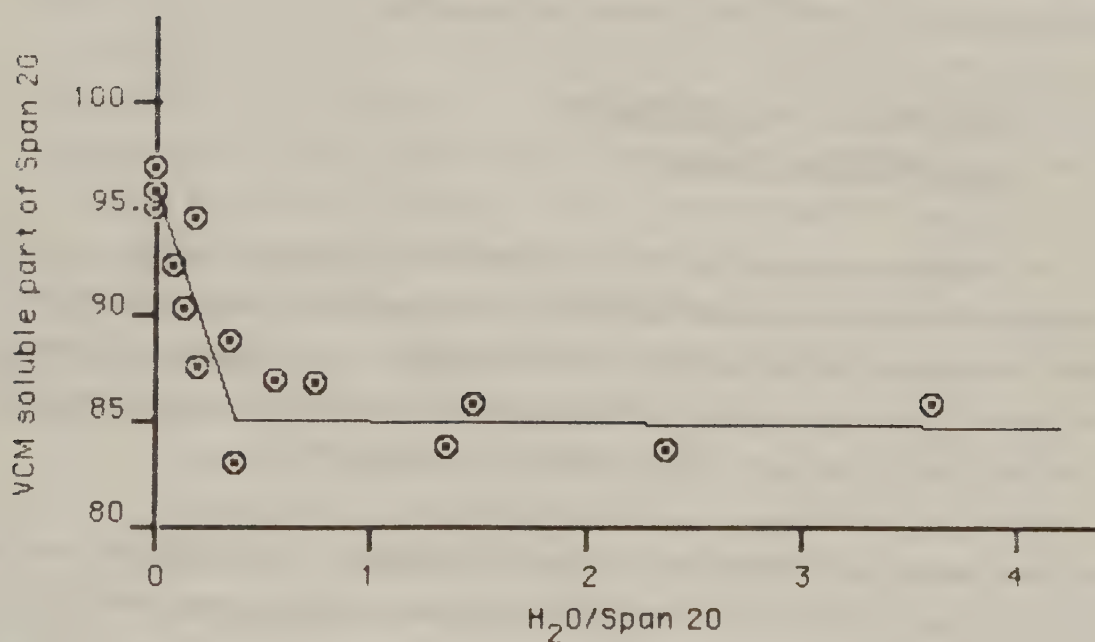


Fig 1. Solubility of Span 20 in VCM in the presence of water

Analysis of Span 20 in water emulsions showed that about 20% of the Span 20 dissolved in water, with the remainder present as a stable oil in water emulsion. This emulsion-forming ability of Span 20, was not seen

with the pure sorbitan laurates.

3.2 Pure Sorbitan Laurates

The esterification of dianhydrosorbitol resulted in dianhydrosorbitol monolaurate (DSML) and dianhydrosorbitol dilaurate (DSDL) (Fig 2). The melting point of the DSDL was 50-53 C. The (DSML) did not crystallize even though it was shown to be the purer product.

Esterification of the mono-anhydrosorbitol gave two mono-lauric fractions, with trace amounts of a dilaurate. One of the monolaurates was identified as anhydrosorbitol 6-laurate (AS6L) ($T_m=48-50$ C) while the other fraction probably was a mixture of the 2, 3 and 5 mono-substituted laurate. (ASML) ($T_m= 46-47$ C). The two fractions of the mono-anhydrosorbitol were not completely separated on the silica column, they had very similar retention times on the gas chromatograph, as well.

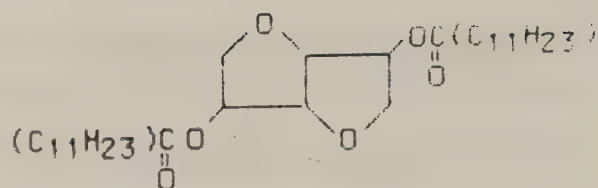
3.3 Bulk Polymerizations

Addition of DSLM to the bulk polymerization of VCM gave an increased number of particles, similar to the effect seen with Span 20 (Fig 3). The results from Span 20 experiments were more scattered than those with DSML. This scatter could be due to slight differences in the water concentration which could greatly alter Span 20 behaviour, due to the complicated Span /water/VCM relationship (see above). DSML is insoluble in water and should thus be less sensitive towards differences in water concentrations.

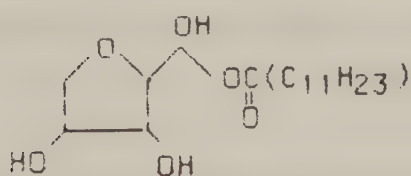
Fig 3 reveal that Span 20 is more efficient in increasing the particle number than pure DSML. It follows that the composition of chemicals in the commercial surfactant more effectively destabilizes the primary particles than does pure DSML. This increased destabilization must be due to some



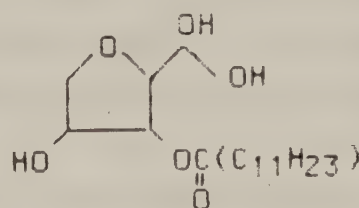
1,4;3,6 Dianhydrosorbitol
monolaurate



1,4;3,6 Dianhydrosorbitol
dilaurate



1,4 anhydrosorbitol
6 laurate



1,4 anhydrosorbitol
2 laurate

Fig 2. Structural formulas for the
synthesized chemicals

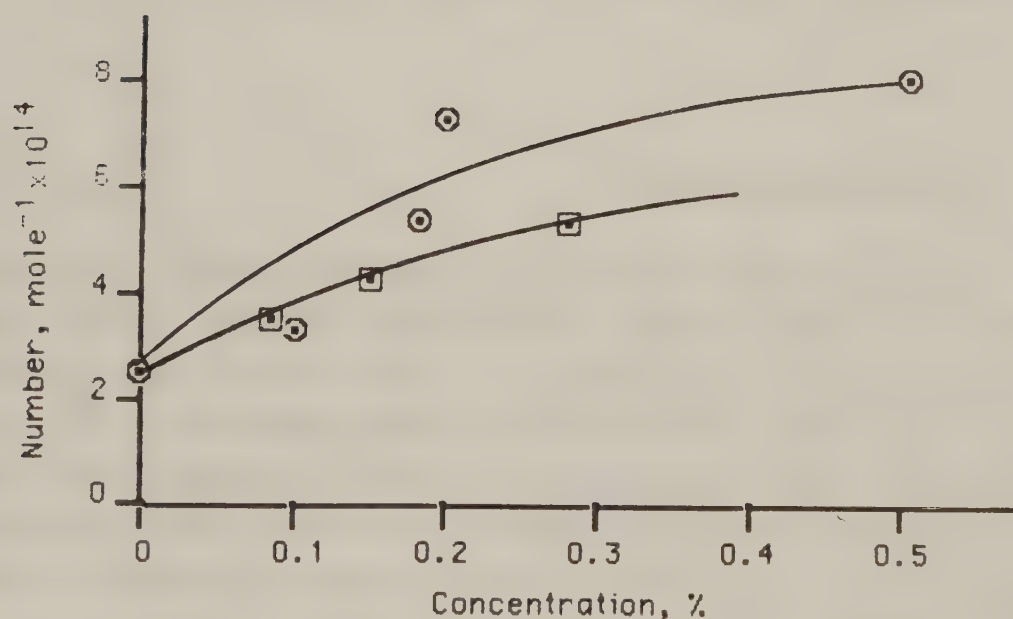


Fig 3. Number of primary particles at 2%
conversion with addition of (○) Span 20 and
(Δ) 1,4-;3,6- di-anhydrosorbitol mono-
laurate (DSML). Agitator tip speed 1.5 m/s.

other components present in Span 20. However, the difference can not be explained by the presence of the other sorbitan laurates which were synthesized (Table 1). Table 1 shows that DSDL and ASML have even a lower efficiency than the DSML; they produce both larger and hence fewer particles. The AS6L had the strongest effect among the pure sorbitan laurates, with an efficiency almost as large as that of Span 20.

TABLE 1

Particle mean diameter (d), number of nucleated particles (N) and the relation between specific surface measured by BET and calculated from particle size. Samples was taken at 2% conversion and polymerized with agitator tip speed of 1.5 m/s.

Chemical	Conc. %	d μm	$N \times 10^{14}$ mol^{-1}	BET Calc. surf
none	----	0.18	2.3	0.86
Span 20	0.14	0.13	5.8	0.50
DSML	0.12	0.15	4.5	0.61
DSDL	0.12	0.18	2.5	0.73
AS6L	0.12	0.14	5.5	0.57
ASML	0.13	0.16	3.6	0.62

The relation between the specific surface measured by BET and that calculated from the particle size, shown in Table 1, is a measure of the particle fusion. This fusion process will eventually lead to the complete disappearance of these small primary particles (4). It is seen that the degree of fusion increases with decreasing particles size.

The effects reached by Span 20 can not totally be explained by the sorbitan laurates synthesized in this study. The four chemicals synthesized should make up the major part of the Span 20 sorbitan laurate

content; results indicate that the laurates were not cause of the Span 20 increased efficiency.

3.3 Conductivity measurments

The electrical conductivity of the distilled VCM was about 8 nS/cm. This value could vary considerably between different runs. Using this conductivity value the ionic strength of the pure VCM was estimated to about $1 \mu\text{mol}/\text{dm}^3$ (11). Adding Span 20 to the VCM led to an increase in the conductivity (Fig. 4), an effect which must be caused by an ionically dissociated substance in the Span 20. A pure sorbitan laurate (DSML) showed no increase in the conductivity at additions of 0.37 and 1 mg DSML per g VCM, suggesting that the ionic species in Span 20 must be an impurity, perhaps some remainder of the esterification catalyst.

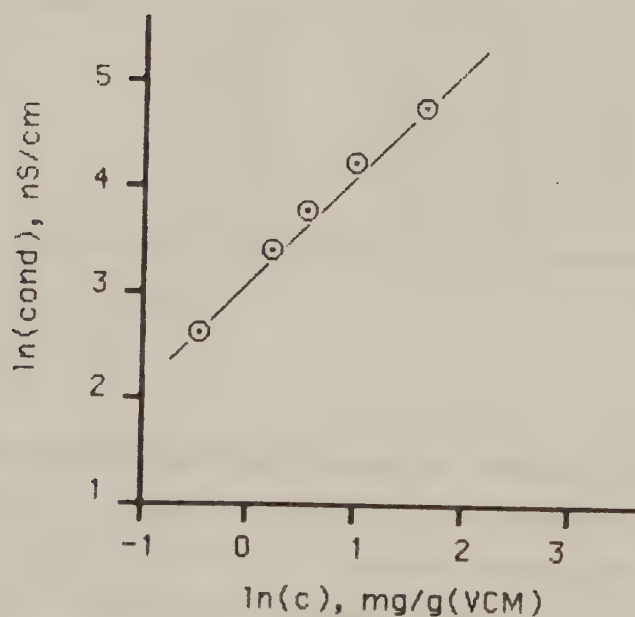


Fig 4. Conductivity of vinyl chloride on addition of Span 20. The given conductivity values are the difference between pure VCM and solution conductivity.

For a completely dissociated salt a plot of log concentration vs. log conductivity has a slope of unity. The slope of the Span 20 conductivity line in Fig 4 is 0.98, which shows that the electrolyte is almost completely dissociated. Other known compounds dissociating in VCM are some tetrabutyl ammonium salts (11). If the ionic mobility and valence of the unknown electrolyte in Span 20 were the same as for tetrabutyl ammonium tetrafluoroborate, could the concentration of the unknown electrolyte in Span 20 be estimated to about 20 mmol/cm³. The ionic strength in the monomer have determining importance for the particle size, as the primary particles are electrostatically stabilized (9,10,11). Increase in the ionic strength by addition of Span 20 will decrease the primary particle stability (and size) by a salting out effect. Addition of 0.28 mmol/dm³ of tetrabutylammonium chloride to a VCM bulk polymerization decreased the particle size from 0.18 to 0.15 μ m (11).

The decreased particle stability on addition of Span 20 was probably a combined effect of surface active processes and the effect of ionic species in the surfactant.

4. ACKNOWLEDGEMENT

We would like to thank Dr Sigfried Svensson of Lund University for his help with the synthetic and analytical work and Dr Guido Bognolo of ICI Speciality Chemicals for supplying us with chemicals. We further wish to thank Samuel Kiuru of Lund University, who skillfully made the BET measurements.

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"Primary Particle Stability in Bulk Polymerization of Vinyl Chloride"
To be published

PRIMARY PARTICLE STABILITY IN BULK POLYMERIZATION OF VINYL CHLORIDE AT HIGH IONIC STRENGTH.

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ABSTRACT

Tetrabutyl ammonium tetrafluoroborate and tetrabutyl ammonium chloride dis- sociate completely in vinyl chloride (VCM). These salts, when added to colloidal dispersions of PVC primary particles in VCM prepared by bulk polymerization, cause the particles to flocculate, showing that the primary particles were electrostatically stabilized.

When bulk polymerizations were carried out in the presence of the same quarternary ammonium salts, smaller primary particles were obtained than in additive-free polymerizations. Addition of tetrabutylammonium tetrafluoroborate to a suspension polymerization increased the porosity of the resin.

INTRODUCTION

In bulk and suspension polymerization of vinyl chloride monomer (VCM) the polymer precipitates in the form of small particles as soon as polymerization starts. This is due to the low solubility of the polymer in VCM. The smallest stable particles observed have a size of about 100 nm, and are known as primary particles. These particles are colloidally stable for only a limited period after their formation. The stability of the primary particles decreases during particle growth (4,7) and the particles agglomerates when they reach a certain size. The point at which agglomeration begins depends on the reaction conditions (1,2). Particle growth is rapid during the period of colloidal stability, but very low after agglomeration (3). Thus, the presence of small, agglomerated primary particles indicates an early agglomeration of particles with a low stability

Several studies have shown that the primary particles are negatively charged (4,5), indicating that perhaps the particles are electrostatically stabilized. Electrostatically stabilized particles would be sensitive to electrolytes dissolved in the monomer. A separate study (6) showed that electrolytes present as impurities in the surfactant Span 20 may destabilize the primary particles. The purpose of this paper is to further explore the relationship between particle stability and electrolyte concentration.

EXPERIMENTAL

The polymerization experiments were made in a 200 ml glass-walled reactor with an enameled stainless steel top and bottom. The conversion, particle size and particle number were measured as described in previous papers (2,3). For measurements of the electrical conductivity of VCM two cylindrical electrodes were mounted inside the

reactor. Each electrode had a surface area of about 80 cm^2 . The distance between the electrode surfaces was 3 mm. The cell constant was determined by comparison with a calibrated cell and was found to be 0.0024 cm^{-1} . The conductivity was measured at 1 kHz with a Metrohm Herisau conductimeter E527, an instrument which automatically compensated for the large cell capacitance, enabling conductivity measurements of down to 2.4 nS/cm to be done.

Vinyl chloride, kindly supplied by Kema Nord Plast AB (presently Norsk Hydro Plast AB), was distilled twice and the permanent gases were vented before use. The tetrabutyl ammonium tetrafluoroborate (Bu_4NBF_4) and tetrabutyl ammonium chloride (Bu_4NCl), were used as received from Fluka AG. They had a moisture content of less than 3 per cent.

RESULTS AND DISCUSSION

Dissociating salts

The quarternary ammonium salts Bu_4NBF_4 and Bu_4NCl dissolved readily in VCM. The conductivity of the VCM solutions of these salts are given in Fig.1 as the difference between the conductivity of the salt solutions (k) and that of pure VCM as measured before addition of the electrolytes (k_0). In this way, variations in the pure VCM conductivity, which ranged from 2.4 nS/cm to 11 nS/cm in the different experiments, were compensated for. The fact that plots of $\ln(c)$ vs. $\ln(k-k_0)$ gave lines with unit slopes shows that the salts were completely dissociated.

The chloride salt had a lower conductivity than the fluoroborate salt. This was unexpected, since the smaller Cl^- ion should have a higher mobility and thus a higher conductivity than the larger tetrafluoroborate ion. The low mobility of the Cl^- ion must be due to a better solvation of

the Cl^- ions.

The conductivity of Bu_4NBF_4 deviates from linearity at concentrations below 0.3 m mole/l (Fig 1). The deviation at these low concentrations was reproducible. At a concentration of 50 $\mu\text{mol/l}$, the difference between the extrapolated line and the measured conductivity was 49 nS/cm, whereas, at the lowest concentration, about 15 $\mu\text{mol/l}$, the difference was 28 nS/cm. In other words, the observed conductivity at 15 $\mu\text{mol/l}$ was more than 2.5 times that corresponding to the linear correlation. This deviation from a linearity at low concentrations is not understood.

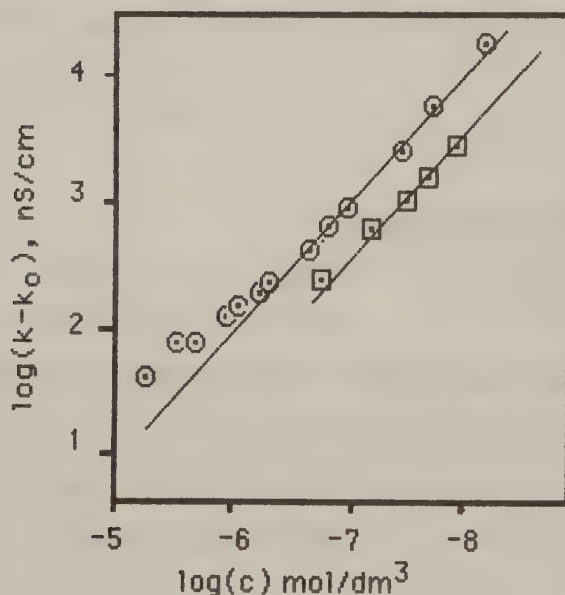


Fig 1. Electrical conductivity of VCM containing (O) Bu_4NBF_4 and (□) Bu_4NCl .

The electrical conductivity of pure VCM, which averaged about 8 nS/cm, must be due to the presense of ionic species in the monomer. Extrapolating the conductivity values in Fig.1 to that of the pure VCM indicates that the concentration of dissociated electrolytes in the pure monomer was about $1 \mu\text{mol/dm}^3$, assuming the same ionic mobilities as

that of Bu_4NBF_4 . The ionic species in the pure monomer probably were by-products formed during the monomer synthesis. Tests with monomer dried over P_2O_5 showed no change in conductivity, indicating that the conductivity of VCM is not related to the monomer water concentration.

Quiescent bulk polymerizations

VCM was polymerized to about 0.1% conversion, at 40 C in a PVC coated glass flask without agitation, using dicetylperoxi dicarbonate as initiator. The flask was then cooled to 20 C. The primary particles formed remained colloidally dispersed and stable in the VCM phase, provided that the flask was not shaken.

Addition of a Bu_4NBF_4 solution to the dispersed primary particles in the flask (at 20 C) initiated a fast flocculation of the particles. The critical flocculation concentration was found to be between 7 and 10 mmol/l for this 1:1 electrolyte. The appearance of a critical flocculation concentration confirms that the particles were electrostatically stabilized.

Agitated bulk polymerizations

Polymerization of VCM in the presence of Bu_4NBF_4 resulted in the formation of small primary particles (Table 1). Small primary particles are obtained when the particles agglomerate at a low conversions, which occurs when the particles are destabilized (3). The fact that small particles were obtained during polymerization in the presence of quaternary ammonium salts is further proof that the particles were destabilized by addition of electrolyte. The destabilization was effective at both levels of agitation.

TABLE 1

The effect of Bu_4NBF_4 in bulk polymerization of VCM on primary particle size (d) and number of particles formed (N)

Bu_4NBF_4 % wt	agitation* m/s	conv. %	d μm	$N \times 10^{-14}$ mol^{-1}
0.00	0.4	1	0.32	0.25
0.02	0.4	1	0.25	0.65
0.20	0.4	1.4	0.10	9.00
0.00	1.5	3	0.18	3.9
0.02	1.5	3	0.12	12.0

* Tip speed of anchor agitator.

Addition of Bu_4NCl to bulk polymerizations also caused a decrease in the primary particle size (Fig 2), in this case from 0.18 μm to 0.13 μm on addition of 0.02 wt% of the salt. A further increase of the salt concentration had little effect on particle size. A sharp decrease in particle size during polymerization in presence of dissociated electrolytes should be expected, since electrostatic stabilization is very sensitive towards the ionic strength (9). However, simple electrostatic theory does not explain why a further decrease in particle size did not occur when the electrolyte concentration was increased above 0.02%. Possibly, a stabilizing mechanism besides the electrostatic one plays a role in the formation of PVC primary particles.

It has been suggested that the stabilizing particle charge is due to absorption of Cl^- ions (5,7,8). According to this suggestion, substances which dissociate into Cl^- ions in the monomer should increase the particle charge. Concentrations of Cl^- ions that are large compared to the normal level, but much smaller than that required to coagulate the primary particles, should produce primary particles with increased stability. This increase in stability should result in the formation of larger primary particles. However, at the lowest Cl^- ion concentration tested, 10 nmol/l, which should fulfill the above requirements, no

increase in particle size was observed. The absence of a stability increase in this experiment implies that the particle charge was not increased by adding chlorine ions. Therefore, it is not clear that the, absorption of Cl^- ions contributes to particle stability.

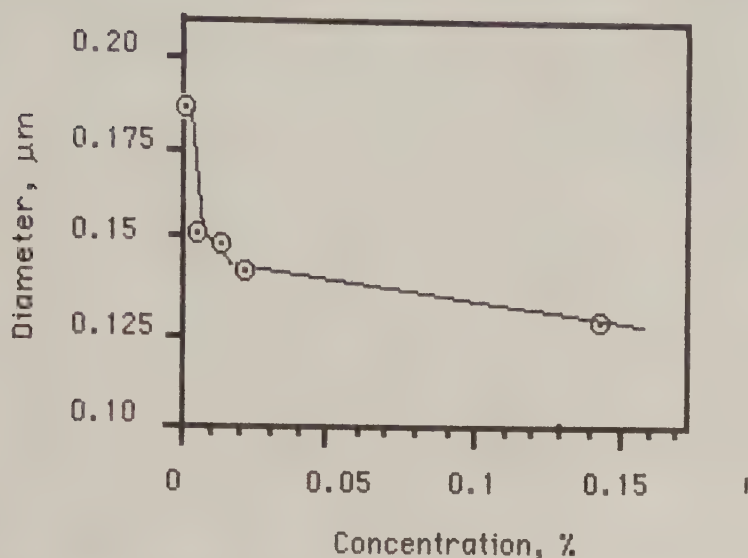


Fig 2. PVC primary particle size at 2% conversion on addition of Bu_4NCl and with an agitator tip speed of 1.5 m/s.

The electrostatic nature of the particles was also evinced by the string structure of agglomerated primary particles, observed in agglomerates formed during polymerization at high agitation rates (Fig 3). The strength of the particle repulsive force depends on the size of the agglomerating particles (7). If the agitation is high the particles agglomerate when they are relatively small in size and still possess a high repulsive electric potential. If two small particles agglomerate, their electric fields are superimposed. The electric field around a particle doublet has a minimum strength at its two end points. A third particle approaching the doublet would therefore tend to agglomerate at one of these points, forming a triplet. By repetition of this process strings of agglomerated primary particles would be formed, like those

shown in Fig 3.

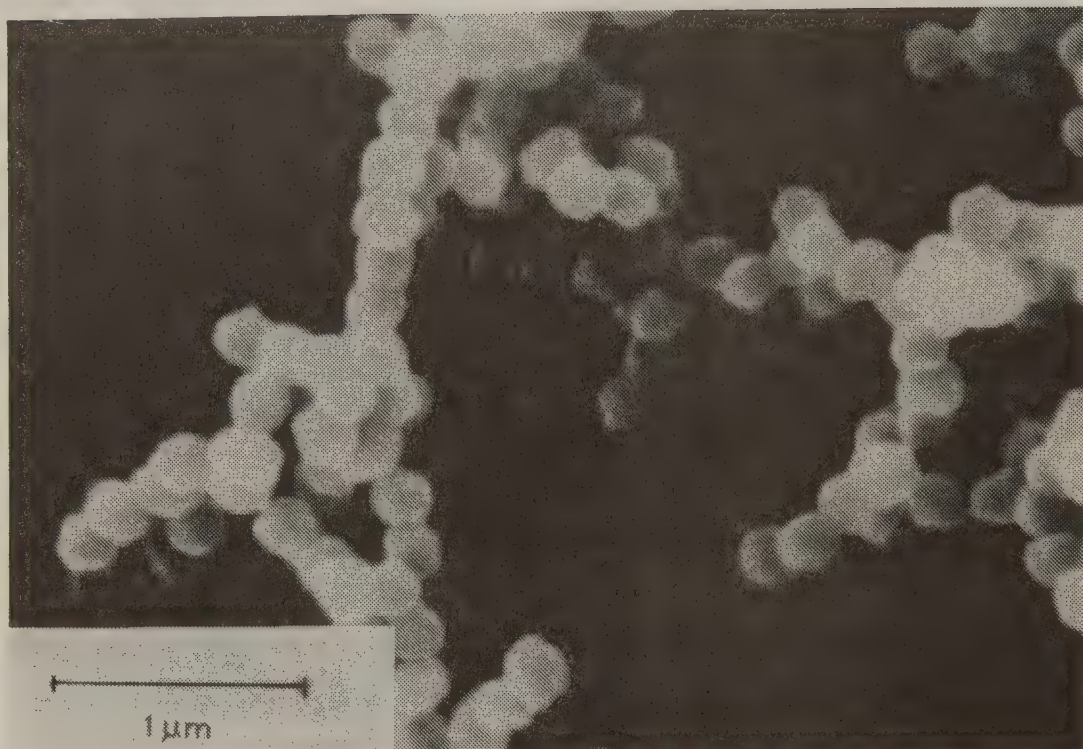


Fig 3. Agglomerated PVC primary particles as observed at 2% conversion, in polymerisation experiments with high agitator speed (tip speed 1.5 m/s).

At slow agitation, the particles will not agglomerate until they reach a larger size, at which their repulsive potential has decreased to a very low value. In this case the superimposed electric field around a doublet would be less assymmetric and much less able to exert a directing influence on agglomeration as in the corresponding case with small particles. Therefore, the buildup of the agglomerates will to a greater extent, be determined by the van der Waals attraction forces, which would favour densely packed structures. As shown in Fig 4, a structure of higher packing density and less string-like formations was produced at low agitation speed.

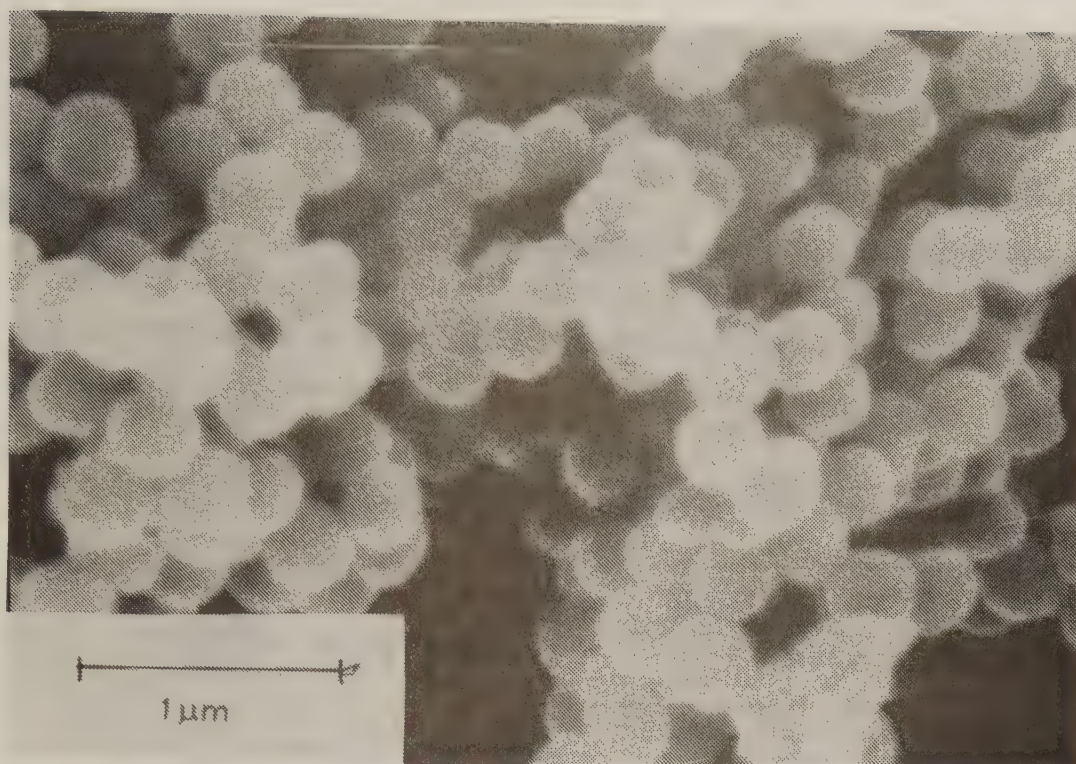


Fig 4. Agglomerated PVC primary particles as observed at 0.5% conversion, in polymerisation experiments with no agitation.

Suspension polymerisations

The relationship between particle size and final resin porosity has been discussed on many occasions. It has been suggested that smaller primary particles would lead to higher porosity, although no experimental material supporting this assumption has been published. In a recent work on bulk polymerization of VCM it was found that the primary particles decreased in size on addition of the nonionic surfactant Span 20 (3). It is possible that the reported effect of Span 20 in suspension polymerization as a porosity increasing agent is caused by a particle size effect.

Suspension polymerizations with addition of 0.02 and 0.2 g of

Bu_4NBF_4 , per 100 g of VCM, gave resins with increased porosity (Table 2). At 0.2% Bu_4NBF_4 the porosity increased by 13 per cent. Also, addition of the salts was followed by an increase in the grain size and gave a broader grain size distribution.

TABLE 2

Properties of fully converted S-PVC on addition of Bu_4NBF_4

Conc. %	Grain size		K-value	Porosity %	bulk density kg/m^3
	average μm	stand dev.			
0.0	120	1.25	67.4	21.4	538
0.02	135	1.40	68.0	23.5	550
0.20	150	1.43	68.0	24.7	532

PVC resin porosity would partly be determined by the forces in the interface between water and monomer as water starts to replace the monomer in the porous system of the grain. The entry of water into the grain structure requires interfacial work. This work is determined by the interfacial tension and the pore size. The pore filling process will give a porosity decreasing pressure gradient at the interface between water and free monomer.

Increasing the monomer ionic strength will destabilize the particles in a suspension polymerization in the same way it does in bulk polymerizations. The destabilized particles will agglomerate at lower conversion and at smaller particle sizes. The increased porosity obtained in suspension polymerization at high ionic strength indicate that an early agglomeration of smaller primary particles promotes formation of porous PVC grains. Whether this is due to the formation of a stronger internal structure, or if the destabilized particles build a skin at the

water VCM interface that is easily penetrated by water is not known.

4. ACKNOWLEDGMENT

Many thanks to Dr. Bengt Jönsson for helping us with the colloid chemical considerations. Thanks are also due to Mr Odd Bjerke and Dr Sven Pettersson at Kema Nobel AB (Norsk Hydro) and to Mr Åsund Rynningen at Norsk Hydro AS.

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COLLOIDAL STABILITY OF PVC PRIMARY PARTICLES IN VINYL CHLORIDE.

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ABSTRACT

The colloidal stability of electrostatically stabilized PVC primary particles, dispersed in vinyl chloride was calculated. The calculations were made using models based on Coulombic interactions and DLVO theory.

A theory of competitive growth of primary particles, based on an analysis of electrostatic interactions during particle growth is described. The mechanism explains why the primary particles have a narrow size distribution.

INTRODUCTION

In bulk and suspension polymerization of vinyl chloride (VCM), small primary particles of poly(vinyl chloride) (PVC) are formed very early during the polymerization. These particles have an initial size of

about $0.1\ \mu\text{m}$ (1), and they are stabilized by electrostatic forces during a certain growth period after their formation (2,3). The size and number of particles formed are closely connected with the particle stability (4,5). A better knowledge of the stability of the primary particles would thus be of practical significance as it might suggest means to control the PVC resin morphology during bulk and suspension polymerization.

During a single polymerization event, starting with the formation of a primary radical by initiator decomposition, about ten PVC molecules are formed closely together in space, due to the chain transfer to monomer (6). The closely spaced polymer molecules agglomerate and form particles which have a radius of about $0.01\ \mu\text{m}$, called basic particles. The small basic particles have no or very limited colloidal stability and agglomerate rapidly forming primary particles. The polymerization continues both in the monomer phase, with formation of new basic particles, and in the polymer phase. The polymerization reactions in the polymer and monomer phases differ both chemically (7) and kinetically (8). After formation the primary particles grow in size but their stability is limited and decreases with particle growth. Hence, at a certain size the particles agglomerate (5,9). Previously, it has been suggested that the number of charges per particle was constant during primary particle growth, leading to a decrease in the particle surface potential and hence a decrease in stability with particle growth (2). The particle charge was assumed to originate from specific sorption of a limited number of charged species, present as impurities in the monomer. More recent investigations have shown that primary particles are formed up to at least 7% conversion, and that the particles formed at these high conversions have the same size and degree of stability as those formed initially (5). This observation is incompatible with the assumption that the stabilizing charges originate from impurities in the monomer. Furthermore, it implies that the assumed constant particle charge during growth period is unlikely.

Previous calculations of primary particle stability were made under the assumption that the Debye-length was $25\mu\text{m}$ (2,10). However, measurements of the electrical conductivity of vinyl chloride have suggested that purified VCM contain dissociated electrolytes at the $1\mu\text{mol/l}$ level (4). Thus, the Debye-length must be considerably shorter than previously estimated. This paper will report calculations of the primary particle stability, based on previous reports of the primary particle electrophoretic mobility (2,5), and Debye-lengths in the range suggested by the conductivity measurements. Part of the calculations are based on the DLVO theory, although the validity of the DLVO theory has not been proven for system with such a low ion concentration as the VCM/PVC system.

THEORY

If the ionic strength in VCM is known, it is possible to calculate the reciprocal Debye-length κ from equation 1.

$$\kappa = \left[\frac{2e^2 N_a c}{\epsilon_0 \epsilon_r kT} \right]^{0.5} \dots\dots\dots (1)$$

where c is the concentration of a completely dissociated 1:1 electrolyte, ϵ_r the relative dielectricity constant, which for VCM is 4.7 (2), N_a Avagadros number, ϵ_0 the dielectric constant in vacuum, k Boltzman's constant and T the temperature in Kelvin.

The particle surface potential ψ can be evaluated from the electrophoretic mobility u using the Hückel equation

$$\psi = \frac{1.5 u \eta}{\epsilon_0 \epsilon_r} \dots\dots\dots (2)$$

where η is the liquid viscosity. The Hückel equation is valid for $\kappa \cdot R < 0.1$, where R is the particle radius. Assuming that the surface of

shear is situated at the particle surface, the particle charge Q can be calculated by

$$Q = \frac{4\pi \epsilon_0 \epsilon_r R \psi}{e} \dots\dots\dots (3)$$

where e is the elementary charge

In this work the particle stability, W_{Tmax} , was estimated as the maximum height of the repulsive energy barrier on particle approach, calculated from $W_T = W_R + W_A$, where W_T is the total interaction energy, W_R the electrostatic repulsion energy and W_A the van der Waals attraction energy.

The attraction energy was calculated as

$$W_A = -\frac{A}{6} \left[\frac{2 R_1 R_2}{s_0^2 + 2R_1 s_0 + 2R_2 s_0} + \frac{2 R_1 R_2}{s_0^2 + 2R_1 s_0 + 2R_2 s_0 + 4R_1 R_2} + \ln \left[\frac{s_0^2 + 2R_1 s_0 + 2R_2 s_0}{s_0^2 + 2R_1 s_0 + 2R_2 s_0 + 4R_1 R_2} \right] \right] \dots\dots (4)$$

where A is the Hamaker constant and s_0 the distance between the interacting surfaces. For the system PVC/VCM the Hamaker constant have been reported to be $5 \times 10^{-21} \text{ J}$ (2).

The repulsive energy was calculated in two different ways depending on the actual Debye-length and particle size. For particle sizes substantially larger than the Debye-length ($(R_1 + R_2 + s_0) \gg 3$) the repulsion energy was calculated according to the DLVO theory

$$W_R = \frac{64\pi R \epsilon_0 \epsilon_r (kT\gamma)^2}{2e^2} \exp(-\chi s_0) \dots\dots\dots(5)$$

where γ is

$$\gamma = \frac{\exp(ze\psi/2kT)-1}{\exp(ze\psi/2kT)+1} \dots\dots\dots(6)$$

For particles smaller than the Debye-length ($\chi(R_1+R_2+s_0) < 1$) the repulsive energy was calculated by a modified Coulombs law

$$W_R = \frac{Q_1 Q_2}{4\pi \epsilon_0 \epsilon_r (1+\chi R_1)(R_1+R_2+s_0)} \exp(-\chi(R_1+s_0)) \dots\dots\dots(7)$$

The modification accounts for the shielding effect exerted by the counter ions around one of the two charged particles, the second particle being treated as a point charge without counter ions. This modification makes it possible to evaluate the electrostatic repulsion between particles with sizes larger than by Coulombs law. This approach is particularly useful in calculating the interaction energy between a large particle and a small weakly charged particle.

The potential barrier for particles with Debye lengths of values between the values which limit equations 5 and 7 must be calculated numerically from Poisson-Boltzmann equation.

RESULTS AND DISCUSSIONS

Debye-length and particle stability

The electrophoretic mobility of colloiddally stable primary particles has been reported as $-1.2 \times 10^{-4} \text{ m}^2 \text{V}^{-1} \text{s}^{-1}$ (2) and $-1.5 \times 10^{-4} \text{ m}^2 \text{V}^{-1} \text{s}^{-1}$ (3), corresponding to a ψ potential of -80 and -100 mV, respectively. In the first investigation the particle radius was 0.15 μm (2), while the second investigation do not state the particle size. Considering experimental difficulties, the agreement between the two

independent investigations is good.

The concentration of electrolyte in pure VCM was estimated to be between $1 \cdot 10^{-7}$ – $1 \cdot 10^{-6}$ mole/l. These values were found by comparing the electrical conductivity of pure VCM with that of VCM solutions of tetrabutyl ammonium tetrafluoroborate (4). The calculated concentrations of electrolyte in VCM correspond to a reciprocal Debye-length between 6×10^6 to $4 \times 10^7 \text{ m}^{-1}$.

Since the Debye-length is of the same magnitude as the particle size, the particle stability should be expected to be sensitive towards changes in the Debye-length. However, if a constant surface potential is assumed, this is not the case. The protective energy barrier for interaction between two $0.15 \mu\text{m}$ particles with surface potentials of -80 mV calculated for κ values from $0.1 \times 10^7 \text{ m}^{-1}$ to $10 \times 10^7 \text{ m}^{-1}$ is given in Fig 1. The shadowed area in Fig 1 is the area where neither eq 5 nor 7 is valid. At the low κ values the Debye-length is larger than the particle size, equation 7 is valid, while at the high κ values, where the Debye length is much smaller than the particle size, the DLVO theory (eq 5) is applicable. The particle stability decreases from 50 kT to about 30 kT over the interval of Debye-lengths covered (Fig 1). This moderate change is due to the sharp increase in the number of charges per particle, as calculated by Hückels equation (eq 3). The number of charges per particle is slightly over-estimated, because the $\kappa \cdot R$ values exceed the allowed limit (eq. 6). However, the number of charges will be over-estimated by less than 20% (11).

The insensitivity of the protective barrier towards changes in the Debye-length, as seen in Figure 1, is present only at constant particle potential. If the Debye-length decreases at constant particle charge,

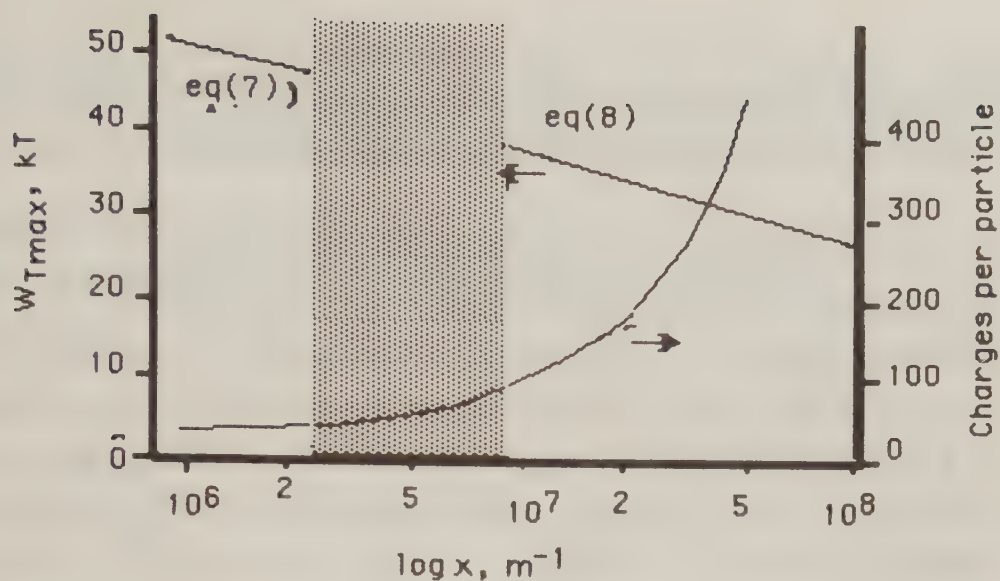


Fig 1. Calculated protective barriers between two charged primary particles both with particle radius $0.15\mu m$ and surface potential $-80 mV$, and the particle charge as a function of Debye-length.

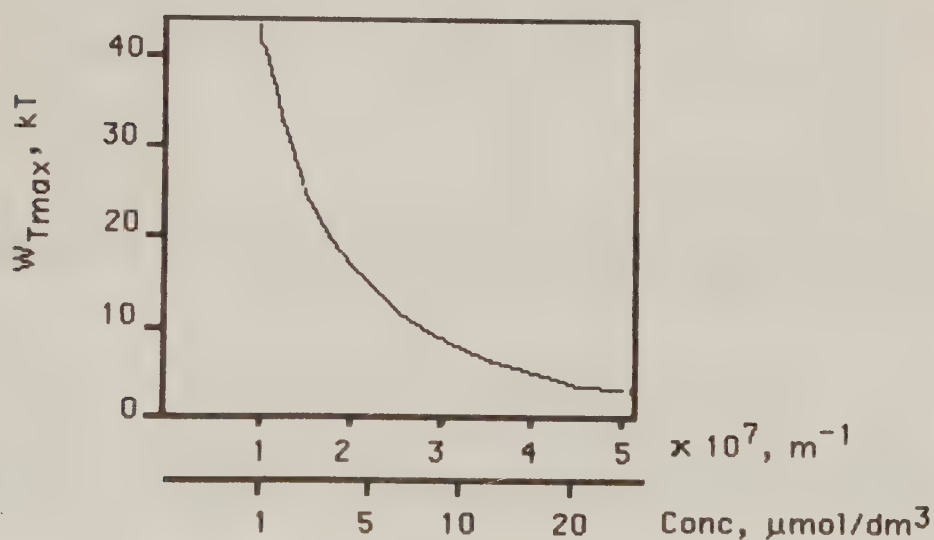


Fig 2. Calculated protective barrier between two charged primary particles both with particle radius $0.15\mu m$ and particle charge of $97 e^-$ as a function of Debye-length.

for example upon addition of electrolytes, then the stability would decrease rapidly with increasing ionic strength (Fig 2).

The limitation of the DLVO theory becomes clear when comparing the distance between charges on the particles with the particle-particle distance at W_{Tmax} . On a primary particle with radius $0.15\text{ }\mu\text{m}$ carrying 100 elementary charges, the charges on the surface will be separated by a distance of $500\text{ }\text{\AA}$, assuming that all of the charges are concentrated on the particle surface. This distance of $500\text{ }\text{\AA}$ should be compared with the $50\text{ }\text{\AA}$ distance at which the maximum interaction energy occurs. Seen from a distance of $50\text{ }\text{\AA}$ the particle surface will show large local variations in the electrical potential, and will not appear as a surface with equal potential, as required by equation 5 and 6. The very low counterion concentration presents another difficulty in applying the DLVO theory, which assumes a continuous ion distribution. The repulsion energy calculations based on the Coulombic interaction are not affected by the low charge concentration on the particle surface, as the theory requires that the charges on the particle are symmetrically distributed around the particle centre. As seen in Fig 1 the stabilities evaluated by eqs. 5 and 7 are of the same order of magnitude and show the same trends in the change of stability. This correspondence suggests that the different errors present in the DLVO theory balance each other giving a repulsion evaluation near the true value.

The particle colloidal stability was found to decrease almost linearly with decrease in particle potential (Fig 3). The behaviour was similar for small and large Debye-lengths as calculated by eq 5 and 7.

Particle size and colloidal stability

Experimental observations show that particles with radii of $0.15\text{ }\mu\text{m}$ have limited colloidal stability, and are shear sensitive (9,12). The calculated stability is about 40 kT , which compared to the experimentally determined electrophoretic mobilities, may seem to be

very high for particles apparently weakly stabilized. However, such high potential barriers may be needed to prevent coagulation in liquids of low viscosity such as VCM, which has a viscosity of 0.2 cP.

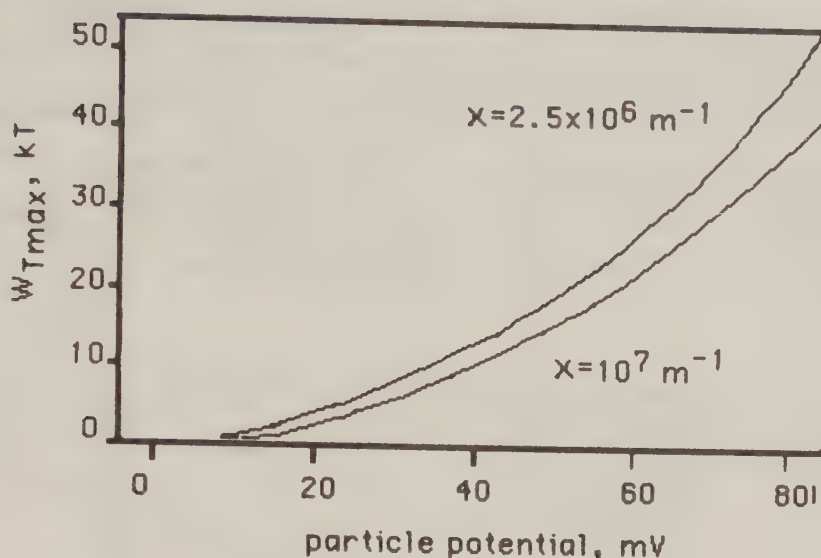


Fig 3. Calculated protective barriers for the interaction between two particles, both of radius $0.15 \mu\text{m}$ as a function of particle potential, with $x = 1 \times 10^7 \text{ m}^{-1}$ and $2.5 \times 10^6 \text{ m}^{-1}$.

It is most likely that the stabilizing charges are produced during polymerization (5). Some results indicate that the charges developed during bulk polymerization are bound to the polymer matrix (13). The production of HCl during radical transfer to polymer previously has been suggested to be a possible source of charged species (5). Charges produced as a consequence of side reactions during polymerization normally would mean that the number of charges increased proportionally to the particle volume. However, this proportional increase may not be the case if the rate of the charge producing reaction changes with particle size. Such a change might be due to differences between the monomer and polymer phase reactions.

To investigate the conditions for particle stability, calculations using different relations between particle charge and particle size were

made. The particle charge was assumed to change with particle size according to $Q \sim R^p$ where p varied between 0 and 2. The total particle charge was chosen so that a particle with a radius $0.15 \mu\text{m}$ had a surface potential of -80 mV . This relation between particle size and charge is not a description of the real charge-size relationship, but a model for calculational purposes only. For p values of 0 to 0.5, the potential barrier was high for small particle sizes and decreased rapidly with particle growth (Fig 4). The interaction energy for very small particles could not be estimated, because the maximum interaction energy was reached at very short distances.

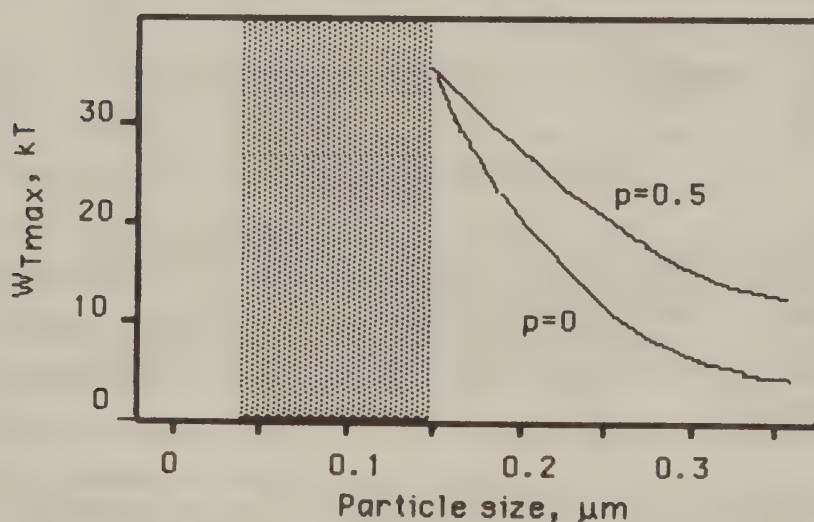


Fig 4. Calculated protective barrier for the interaction between two primary particles, where the charge varies as $Q \sim R^p$ for $p=0$ and 0.5, and at $\kappa = 1 \times 10^7 \text{ m}^{-1}$, and with the surface potential -80 mV at $R=0.15 \mu\text{m}$.

For p values of 1, 1.5 and 2, the particle potential barrier increases during growth for particles of small sizes (fig 5). For $p=1.5$ and 2 the barrier continued to increase for particles of larger sizes. For the case of $p=1$, the barrier reached a maximum, and subsequently decreased slowly. Taking only the potential barriers given in Fig 5 as the measure of particle stability, it could be concluded that the particle

charge must increase at the rate of R^1 or more slowly, if the particles were to lose stability with growth. However, the calculated potential barriers do not account for all mechanisms which affect particle stability. Primarily, the increase of distance between charges on the particle surface with particle growth when p is less than 2 is not accounted for in the calculations. A second factor neglected by the theoretical treatment is the agitation. A large particle in an agitated

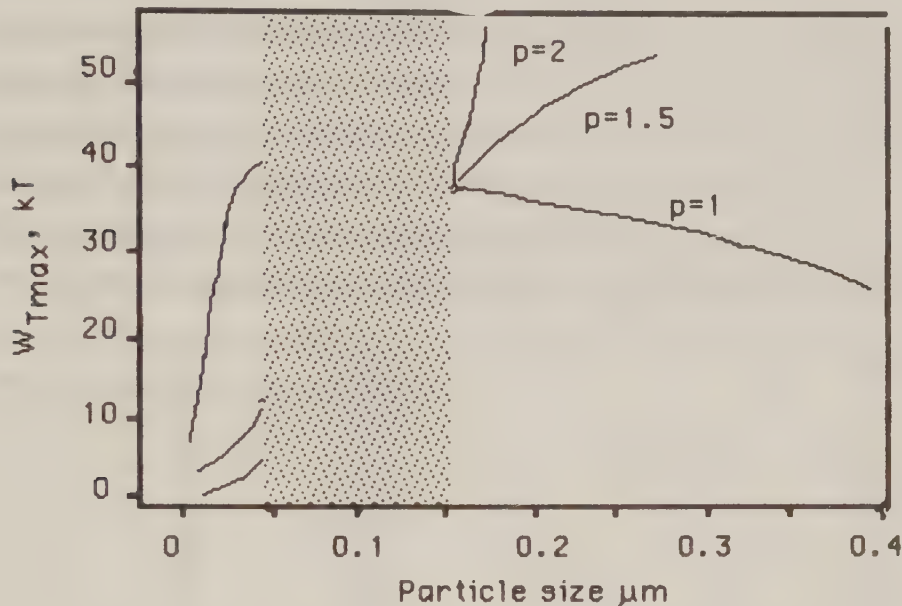


Fig 5. Calculated protective barrier for the interaction between two primary particles, where the charge varies as $Q \sim R^p$ for $p=1.5$ and 2, and at $\chi = 1 \times 10^7 \text{ m}^{-1}$, and with the surface potential -80 mV at $R=0.15 \mu m$.

reactor will be more influenced by the shear field than a small particle. The effect on the particle by the agitation depends on the kinetic energy received by the particles from the shear field. The particle kinetic energy is dependent on particle mass and the particle relative velocities. The particle mass increases with the cube of particle size. Since the particle relative velocity probably increases with particle size, the particle kinetic energy is increasing with at least the cube of

particle size. If the kinetic energy caused by the agitation increases more rapidly with size than does the energy barrier (cf Fig 4), particles with a charge increase as calculated by p 1.5 and 2 may also lose stability on growth.

Competitive growth and particle size distribution

A striking feature of bulk polymerization of VCM is the narrow size distribution of the primary particles (Fig 6). The presence of equally sized particles implies that there must be a mechanism suppressing the natural deviation in particle size. One explanation for the formation of equally sized particles is that electrostatic effects control the particle growth. At low conversion, the primary particles grow, primarily by

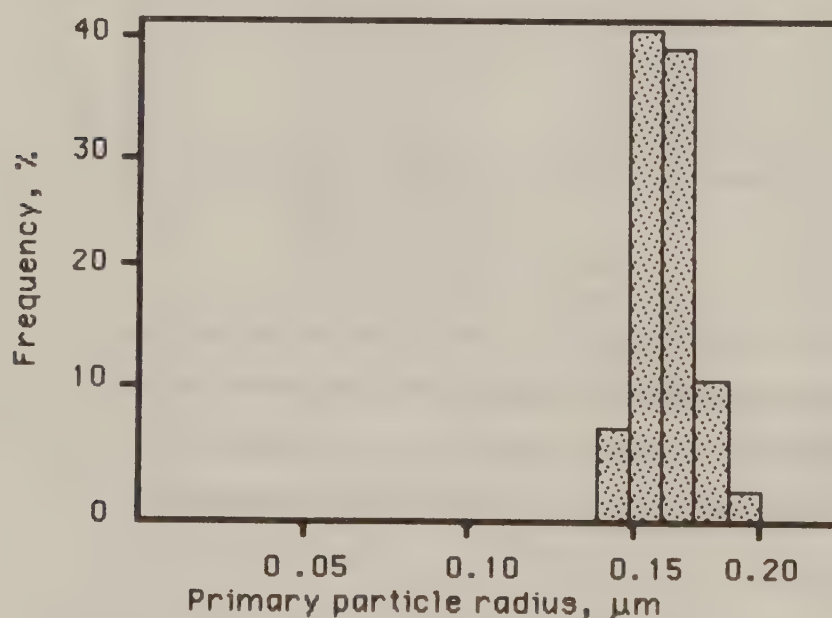


Fig 6. Primary particle size distribution at 0.5% conversion in a non-agitated bulk polymerizations of VCM at 60 C.

absorption of newly formed basic particles. At least some of these basic particles would carry one or a few charges. A single charge on the basic particle is far too weak to prevent it from coagulating with a primary

particle, but the charged basic particle will certainly interact with the highly charged primary particle. Similar mechanisms for explaining particle nucleation have previously been put forth for polystyren emulsion polymerizations (14).

Calculated interaction energies between a small particle of radius of $0.01\ \mu\text{m}$ carrying one elementary charge and a primary particle eq 7 should give reliable results for primary particle sizes less than the Debye-length ($R < 0.1\ \mu\text{m}$). The calculations revealed that the interaction energy between a basic particle and the small primary particle with constant charge ($p=0$) was higher than between a basic particle and the large primary particle (Fig 7). Clearly, such behaviour can not result in the development of equally sized particles, since the basic particles would more readily agglomerate with large primary particles than with small ones. Any difference in the primary particle size would be increase during polymerization.

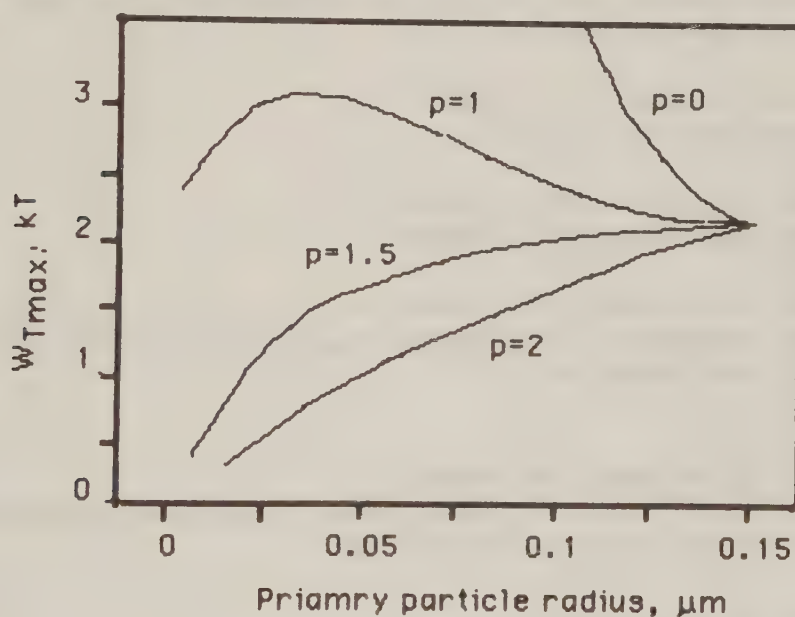


Fig 7. Protective energy barrier between a basic particle ($R=0.01\ \mu\text{m}$, $Q=1e^-$) and a primary particle varying size, with a surface potential $-80\ \text{mV}$ at $R=0.15\ \mu\text{m}$ and $Q(R)=RP$.

For $p=1$, the interaction energy reached a maximum at a primary particle size of about $0.025\ \mu\text{m}$, followed by a slow decrease in stability. For p values of 1.5 and 2 the interaction energy between a basic particle and a large primary particle was higher than between a basic particle and a small primary particle. Such conditions would lead to a competitive growth, as the basic particles now would more readily agglomerate with a small primary particle than with a large one. The growth rate for small primary particles will thus be larger than for the large primary particles, leading ultimately to equal sizes.

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ELECTRICAL CONDUCTIVITY IN VINYL CHLORIDE

by

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ABSTRACT

Vinyl chloride of good polymerization quality showed electrical conductivity. The ionic strength of VCM purified by distillation appears to be independent of temperature in the range between 20 and 40 C, and to decrease at higher temperatures.

Measurements during bulk polymerization of VCM showed that the conductivity decreased at least initially with conversion. Other results indicated that electrolytically active species were formed during the polymerization and trapped in the polymer matrix.

INTRODUCTION.

Bulk and suspension polymerization of vinyl chloride (VCM) is a precipitation polymerization which proceeds, at least up to 7 % conversion, through the formation of particles, called primary particles. The primary particles are colloidally stable in the monomer during a short growth period (1). The size and total number of the primary particles formed is determined by their colloidal stability (2). Some results from suspension polymerization indicate that a change in particle stability affects the suspension resin porosity (3).

Measurements of the electrophoretic mobility of the particles and dispersion stability experiments at high ion strength have shown that the particle stability is due to the presence of negative charges on the particles (3,4,5). It has been suggested that these charges originate from impurities in the VCM phase (4,5). The observations that new primary particles are in fact formed at conversions up to and above 7%, and that these particles have the same stability and size as those initially formed, seem to exclude the possibility that the stabilizing particle charge is due to sorption of a limited amount of impurities present in the monomer (2). Therefore, it is likely that the charged species responsible for the particle stabilization are formed during the polymerization (7).

This paper reports results obtained by measuring the electrical conductivity of vinyl chloride, which may give information about the electrolytic conditions in VCM before and during polymerization.

EXPERIMENTAL

The conductivity measurements were made with a conductivity cell described elsewhere (3). The conductivity cell was mounted inside a 200 ml reactor. The rate of polymerization could be measured by measuring the the temparture increased in the ractor by the polymerization reaction. The change in temperature was never higher then 10 mK (2,8).

The VCM was kindly supplied by Kema Nord Plast AB, and was distilled before use. The tetrahydrofuran (THF) used was of analytical grade and was vacuum distilled before use.

RESULTS AND DISCUSSION

electrolytes in VCM

In a previous publication, it has been reported that the electrical conductivity of redistilled VCM of commercial quality at 20 C is between 2 and 15 nS/cm (3). Further investigations showed that the conductivity of pure VCM decreased with increasing temperature (Fig 1). As seen in Fig 1,

the conductivity decreased slowly in the temperature range from 20 to 50 and more rapidly above 50 C. The conducting species are probably ions which are in equilibrium with ion pairs. The decrease in conductivity on heating may be the result of combined effects of changes in the electrolyte dissociation equilibrium, decrease in monomer viscosity and volume expansion during heating.

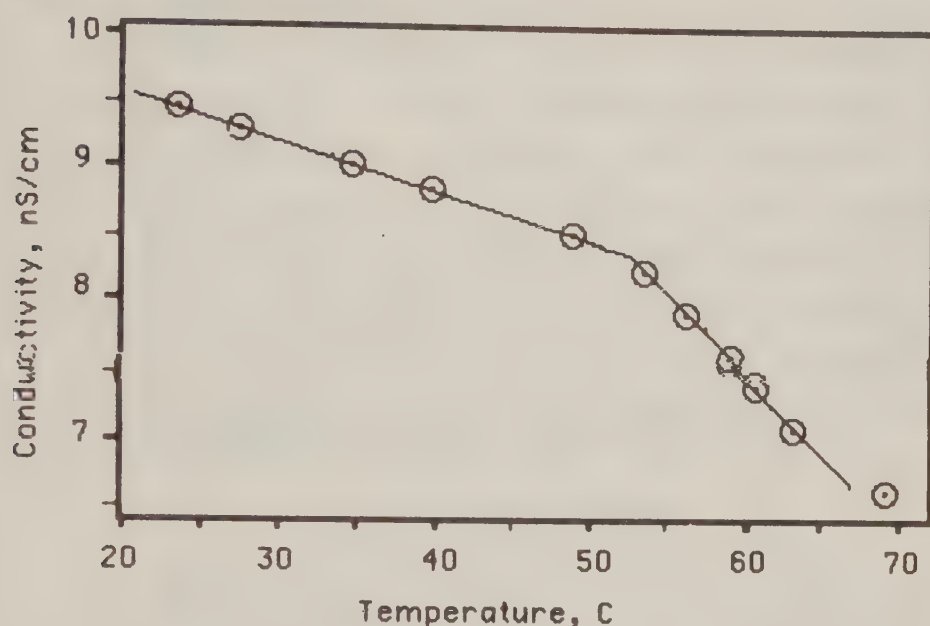


Fig 1. Conductivity in pure VCM

The conductivity data in Fig 1 could be used to calculate the concentration of ionic species in VCM if the ion mobilities were known. From previous measurements of the conductivity k of solutions of tetrabutyl ammonium tetrafluoroborate (Bu_4NBF_4) in VCM (3), the sum of the anion and cation mobilities u can be calculated by $k=C \cdot u$, where C is the total concentration of Bu_4NBF_4 . In this case the average ion mobility value was $8.7 \times 10^{-8} \text{ m}^3 \text{ s}^{-1} \text{ V}^{-1}$, which was calculated from data obtained in the concentration interval 0.3 and 8 mmole/dm³. The change in ion mobility with temperature for a fully dissociated salt can be calculated from the data in Fig 2, giving the conductivity of a 0.3 mmole/dm³ solution of Bu_4NBF_4 in VCM. In these calculations the change in concentration due to the change in VCM density with temperature must be considered (9). Assuming that the ions in freshly distilled VCM change their mobility at temperature

changes by the same rate as Bu_4N^+ and BF_4^- , the relative change in pure VCM ionic strength can be computed from conductivity measurements in Fig 1. The result reveals that the concentration of conducting species per unit volume in pure VCM is almost constant between 20 and 50 C, but decreases at higher temperatures (Fig 3).

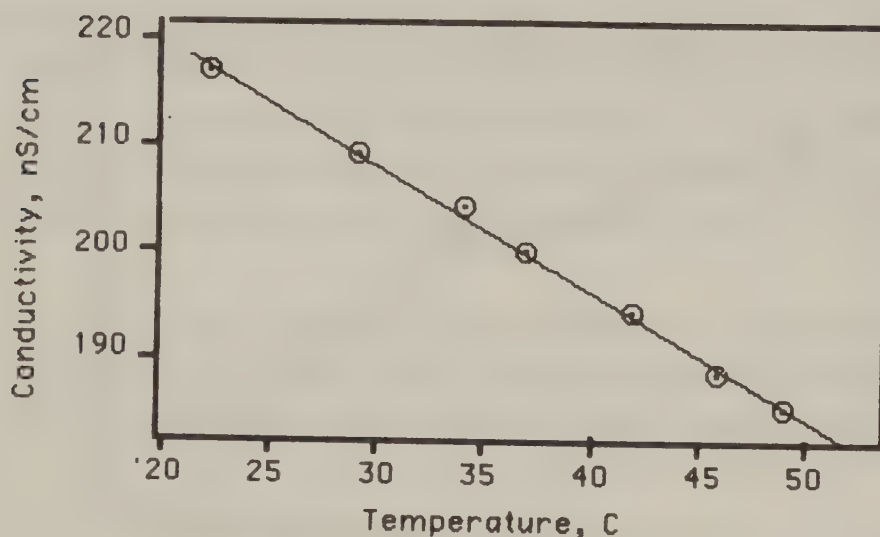


Fig 2. Conductivity of 0.3 mmol/l tetrabutyl ammonium tetrafluoroborate VCM solution.

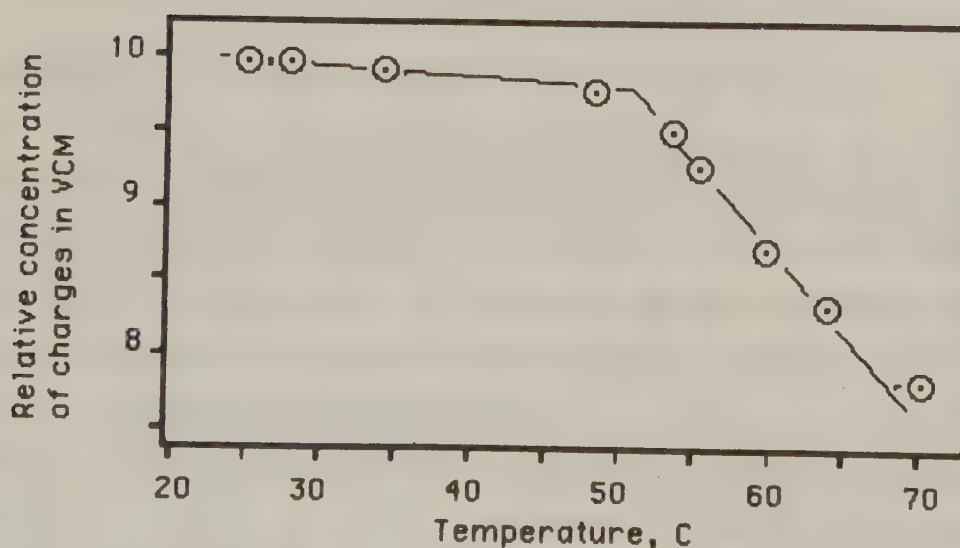


Fig 3. Concentration of charges in pure VCM (arbitrary units)

Electrical conductivity during polymerization

The VCM phase conductivity was also studied during bulk polymerization. The polymerizations were initiated by 0.14 mM dicetyl diperoxi dicarbonate at 39 C. To obtain an even and constant temperature in the reactor, the reactor was agitated with a propeller at high speed. Immediately after the addition of the initiator, the conductivity increased with 0.22 nS/cm to 9.41 nS/cm, during a period of inhibition of the polymerization reaction. As the polymerization reaction started, as indicated by the thermal measurement, the conductivity began to decrease (Fig 4), and reached 2.3 nS/cm at 0.16 % conversion. This decrease was definitely the result of a decrease in the ionic conductivity of the VCM and not caused by polymer precipitation on the electrode surfaces. At the high stirring speed the primary particles started to agglomerate at about 0.14 % conversion. No effect of agglomertaion on the VCM phase conductivity could be observed.

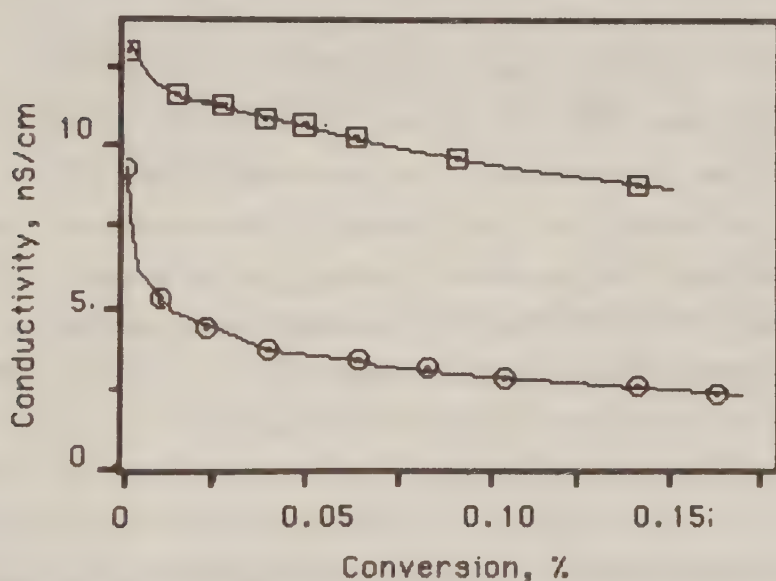


Fig 4. VCM phase conductivity during bulk polymerization of VCM, (○) pure VCM, (□) with 0.05 mmole/l O₂⁻.

The increase in the conductivity during the first inhibited part of the polymerization might be caused partly by small amounts of oxygen, acting

as an inhibitor. Addition of 0.05 mmol/l oxygen to the vinyl chloride before addition of the initiator caused the conductivity to increase with 3.82 nS/cm to 13.1 nS/cm, during the inhibition period (Fig 4). Also in this case the conductivity decreased during polymerization but the conductivity difference between the two polymerizations with and without oxygen increased during polymerization.

To investigate, the conductivity increase during oxygen-inhibition, VCM containing initiator was repeatedly inhibited by addition of oxygen so that no polymerization reaction started. An addition of 0.15 mmole/liter of oxygen gave a 15 nS/cm increase in the conductivity. Additional amounts of oxygen caused no further increase in conductivity. The reaction products from oxygen inhibition of VCM are HCl, CO and formaldehyde (10). Addition of CO increased the VCM conductivity by only 0.5 nS/cm, a limit which was reached at 1 mmol/l of CO, whereas HCl caused an increase of about 20 nS/cm, a limit which was reached already at concentrations below 0.05 mmol/l. Some results obtained at temperatures below room temperature, show that the conductivity of VCM changes during a certain time period after addition of HCl. The conductivity decreased to almost 50% of its value observed immediately after HCl addition. This occurred over a period of 1-2 minutes. At higher temperatures, this decrease in conductivity occurred very rapidly, so that only the lower conductivity value was measured. These observations indicate that the effect of HCl on the conductivity of VCM is not due to H^+ and Cl^- , but rather that HCl participates in a reaction in VCM, and the reaction products dissociate in the VCM.

Electrolytes in the polymer

As previously stated, the electrolytes produced during the inhibited part of the polymerization can not be the only substance which gives electrostatic charges to the particles. Electrolytes giving the stabilizing charges are most likely produced during the polymerization. Such charges seem to be bound to the polymer phase, since no increase in the monomer phase conductivity was observed during polymerization (Fig 4). The assumption that charged species are trapped in the polymer phase (7), explains why no measurable increase in the monomer phase conductivity

was seen. In order to test this suggestion, separate bulk polymerizations were made. In these experiments, samples were withdrawn at various reaction times and dissolved in THF. The electrolytic activity was tested by measuring the conductivity of the THF solution.

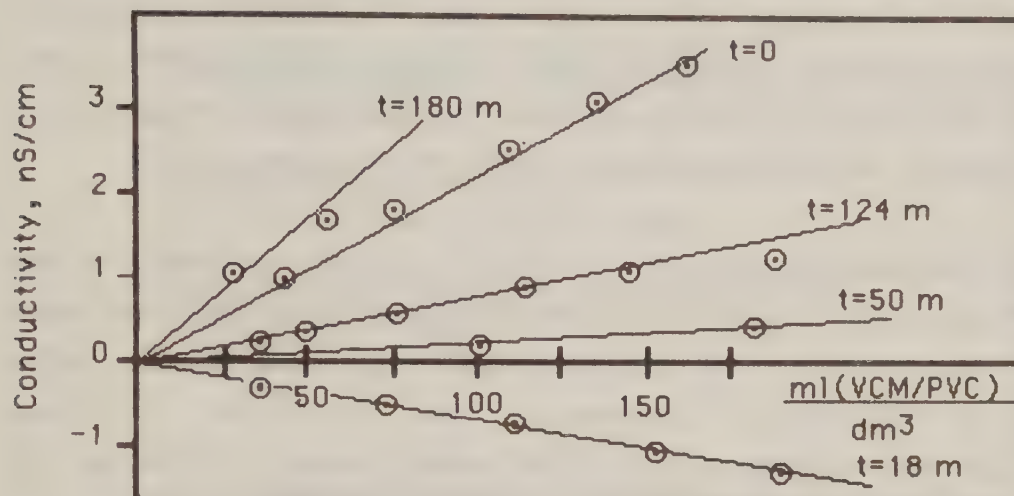


Fig 5. Conductivity of THF solutions of VCM bulk polymerisate. Conductivities as differences between solution conductivities (k) and pure THF conductivities (k_0).

The bulk polymerizations were carried out in a pressurized burette at 40 C with 0.4 mmole/liter of dicetyl diperoxi dicarbonate as initiator. The reactions was stopped at a predetermined times by cooling to 20 C. The amount of electrolyte in the monomer/polymer mixture was measured by adding the PVC/VCM suspension to the conductometer cell, which was filled with THF. The small polymer particles were immediately dissolved in the THF, and the solution conductivity could be measured. Repeated additions of small volumes of the monomer/polymer mixture enabled the relation between the amount of polymer and the conductivity to be evaluated. The slope of the plot of conductivity as a function of added amount of VCM/PVC is a measure of the amount of electrolyte in the polymerization system which can dissociate in THF.

Addition of pure VCM/initiator solution to the THF caused the conductivity to increase, since the conductivity of THF was lower than that of the added VCM ($t=0$ in Fig 5). Addition of a polymer/VCM mixture taken after 18 minutes polymerization gave a solution conductivities which were lower than for the pure THF. The decrease in slope between the lines for $t=0$ and that of $t=18$ minutes (Fig 5) shows that the amount of dissociating electrolyte decreased during the early stages of the polymerization, probably the same effect seen in the VCM phase during early stages of bulk polymerization, when the VCM phase conductivity decreased (Fig.3).

Polymerizations made for 50 minutes showed an increase of the conductivity compared with the 18 minutes polymer. Polymerizations made for 124 minutes and for 180 minutes showed a continued increase in the amount of dissociating electrolytes. The conversions of these polymerizations were not measured, but were estimated to be below 10% conversion for the polymer which had reacted for 180 minutes. The increased conductivity with time showed that electrolytes which could dissociate in THF were formed during polymerization. Whether the same species can dissociate in PVC/VCM systems, and if the dissociating ions are the potential-determining ions on the charged primary particles, can not be concluded from these experiments.

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